

THE PROBLEM OF IDENTIFYING AN ADEQUATE KINETIC EQUATION FOR A CHEMICAL TRANSFORMATION IN THERMAL ANALYSIS

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Additional criteria are suggested for the selection of an adequate function $g(\alpha)$ describing the mechanism of a chemical transformation using the Satava method.

A major task in kinetic analysis is the discovery of the mechanism of a chemical reaction. Information on the reaction path in time and space allows a detailed knowledge of the kinetic relationship and the establishment of a mathematical model of the transformation in the form of a kinetic equation. It should always be kept in mind, however, that the formal applicability of a certain kinetic equation to describe an experimentally obtained kinetic curve is — as a rule — an insufficient criterion. Full evidence of the correct mechanism and of the adequate kinetic equation can only be obtained by a complex study of the chemical transformation, utilizing various physico-chemical and physical techniques to investigate the state of the substances. On the other hand, if the chemical reaction in question cannot be described by the kinetic equation applied, this is sufficient proof that the mechanism on which the equation is based is unsuitable. In this case an analysis of the effects of supplementary agents on the general course of the transformation must be performed. It should be added that the kinetic equation cannot, on principle, cover the whole kinetic curve. There will always exist initial and final sections of the kinetic curve which will not fit the general kinetic relationship. This is particularly sharply observable in the final section of the transformation, where diffusion will retard the course of the reaction. A knowledge of the mechanism of the solid-phase reaction and of the kinetic equation and the kinetic parameters will ultimately be of additional support in the optimization of the technological processes.

In thermoanalytical practice relating to the study of non-isothermal transformations, the Satava method [1] is frequently used to identify the mechanism of the thermal transformation, by seeking the best linearization of the function $\ln g(\alpha)$ vs. $1/T$ by one of the following equations:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{EA}{Ra} \cdot p(x) \quad (2)$$

$$\ln g(\alpha) - \ln p(x) = \ln \frac{AE}{Ra} \quad (3)$$

The symbols used are those generally accepted in the kinetics of non-isothermal transformations. For the function $g(\alpha)$, a set of functions is tried, each function reflecting a particular model (Table 1). However, in practice this method appears rather insensitive to the choice of the function $g_i(\alpha)$, that is, the correlation coefficients for Eq. (3) differ only slightly and are close to those for Eq. (1). Consequently, additional criteria are required to select the correct function $g(\alpha)$ or $f(\alpha)$.

By way of example, we shall examine the introduction of additional criteria, using the experimental data reported in [2] and [3] on the kinetics of the irreversible decomposition of CaC_2O_4 to CaCO_3 . The calculated average values for E and $\ln A$ are listed in Tables 2 and 3. The plot $\ln A$ vs. E (Fig. 1) clearly demonstrates that the average and individual kinetic parameters fit well into the general linear compensation relationship $\log A = 0.068 E - 2.5$. The apparent isokinetic temperature

Table 1

Forms of the functions $f(\alpha)$ and $g(\alpha)$ for different particular reaction mechanisms

	$f(\alpha)$	$g(\alpha)$
D_1	α^{-1}	α^2
D_2	$[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha) + \alpha$
D_3	$(1-\alpha)^{1/3}[-\ln(1-\alpha)]^{-1}$	$[1 - (1-\alpha)^{1/3}]^2$
D_4	$[-\ln(1-\alpha)]^{-1}$	$\left(1 - \frac{2}{3}\alpha\right) - (1-\alpha)^{2/3}$
F_1	$(1-\alpha)$	$[-\ln(1-\alpha)]$
A_2	$(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A_3	$(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
R_1	$(1-\alpha)^{1/3}$	$3[1 - (1-\alpha)^{2/3}]$
R_2	$(1-\alpha)^{1/2}$	$2[1 - (1-\alpha)^{1/2}]$
R_3	$(1-\alpha)^{2/3}$	$\frac{3}{2}[1 - (1-\alpha)^{1/3}]$

Table 2

Average kinetic parameters for the transformation of CaC_2O_4 into CaCO_3 at constant initial mass of the specimen $m = 5 \pm 0.1$ mg and varying heating rates

Parameters	D_1	D_2	D_3	D_4	F_1	A_2	A_3	R_2	R_3
E , kJ/mol	437.7	477.6	529.2	494.5	290.0	137.1	87.3	245.7	258.4
$\lg A$	27.85	30.47	33.59	31.05	18.00	7.17	3.56	14.44	15.21
$\pm \sigma(E)$ kJ/mol	20.2	23.0	28.2	24.4	16.6	8.9	6.0	12.7	14.3
σ , %	4.6	4.8	5.3	5.0	5.7	6.5	6.9	5.2	5.5
ΔE kJ/mol	260.0	283.0	314.0	296.0	175.0	91.3	64.5	153.0	161.0

Note: ΔE was calculated for the temperature $T_x = 769$ K.

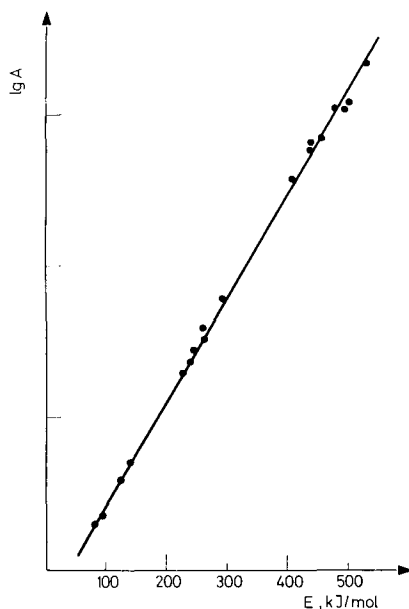


Fig. 1. Compensation effect for the thermal transformation under varied experimental conditions

Table 3

Average kinetic parameters for the transformation of CaC_2O_4 into CaCO_3 at constant heating rate $a = 10^\circ/\text{min}$ and varying initial specimen masses

Parameters	D ₁	D ₂	D ₃	D ₄	F ₁	A ₂	A ₃	R ₂	R ₃
E , kJ/mol	407.3	442.5	487.3	457.2	261.8	124.8	79.1	226.5	237.6
$\lg A$	25.76	28.04	30.68	28.47	16.01	6.27	2.96	13.09	13.73
$\pm \sigma(E)$ kJ/mol	25.0	26.5	28.6	27.2	15.5	7.8	5.2	13.7	14.4
σ , %	6.1	6.0	5.9	5.9	6.0	6.2	6.5	6.1	6.1
ΔE kJ/mol	242.0	264.0	291.0	275.0	160.0	84.7	60.2	143.0	150.0

Note: ΔE was calculated for the temperature $T_x = 769$ K.

T_x is 769K and lies in the range of maximum rates of transformation. The compensation effect observed in this case is apparent in character, since, according to [4], no isokinetic coordinate ($\ln k_x, 1/T_x$) exists. This may also be demonstrated by calculating the free activation energy, using the equation

$$\Delta E = E - RT_x \ln A \quad (4)$$

where T_x is the isokinetic temperature. If this temperature should actually exist, then all values ΔE should be identical. However, this cannot be observed in Tables 2 and 3. Nevertheless, the existing compensation relationship allows forecasting of the activation energy, if the numerical value of the pre-exponential factor A can be theoretically deduced by some means.

A probable additional criterion for the choice of the correct function might be the physically founded value of the pre-exponential factor in the Arrhenius equation, which, in the general case, should correspond in some manner to the actual vibrations of the activated complex ($10^{11} \dots 10^{15} \text{ s}^{-1}$). If this assumption is accepted as starting point, the most probable equations for describing the process of decomposition of CaC_2O_4 to CaCO_3 are F_1 , R_2 and R_3 . Let us consider one other example. In a study of the kinetics of the phase transition of aragonite into calcite under non-isothermal conditions Tolokonnikova et al. [5] found that, from the view of linearity, equations F_1 and A_2 represent the optimum. The calculated kinetic parameters are

$$E = 49 \text{ kcal/mol and } A = 1.6 \cdot 10^{14} \text{ s}^{-1} \quad (F_1)$$

and
$$E = 22 \text{ kcal/mol and } A = 2 \cdot 10^5 \text{ s}^{-1} \quad (A_2),$$

respectively.

Since only one of the two mechanisms can be correct, those authors decided in favour of F_1 , taking into account the above criterion regarding the value of the pre-exponential factor A .

As a third criterion in the choice of the function $g(\alpha)$, we suggest the value of the conversion α_m at the point of the maximum rate of transformation, at the temperature T_m . By integration of the starting equation (1) according to [6], one obtains

$$g(\alpha) = \frac{A}{a} \cdot \frac{RT^2}{E + 2RT} \exp\left(\frac{-E}{RT}\right) \quad (5)$$

Analogously to [4], the pre-exponential factor A can be expressed analytically:

$$A = - \frac{Ea}{f^1(\alpha_m) RT_m^2} \cdot \exp \frac{E}{RT_m} \quad (6)$$

where $f^1(\alpha) = \frac{df(\alpha)}{d\alpha}$. Substituting this equation into Eq. (5) and performing the necessary mathematical operations will then yield

$$g(\alpha_m) \cdot f^1(\alpha_m) = \frac{E}{E + 2RT_m} \quad (7)$$

Consequently, a fixed value α_m must correspond to definite values of E and T_m . For kinetic equations of the type $\frac{d\alpha}{dt} = k(1-\alpha)^n$, describing the shift of the interface between the phases, Eq. (7) may be written in the following form:

$$\frac{n[1 - (1 - \alpha_m)^{1-n}]}{(1 - \alpha_m)^{1-n}(1 - n)} = \frac{E}{E + 2RT_m} \quad (8)$$

The value of the fraction $\frac{E}{E + 2RT_m}$ is close to 1, and for the general case, according to [7], Eq. (7) will empirically assume the form

$$1 - \alpha_m = 1.062 n^{1/(1-n)} \quad (9)$$

Therefore, an unequivocal relationship exists between n and α_m , and hence the value $1 - \alpha_m$ for the reaction $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3$ at $n = 0.5$ should be 0.265. If this is in fact the case, then this would appear a further criterion in favour of choosing equation R_2 .

References

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ZUSAMMENFASSUNG — Zusätzliche Kriterien werden zur Auswahl der geeigneten Funktion $g(\alpha)$ zur Beschreibung des Mechanismus der chemischen Umwandlung mit der Satava-Methode vorgeschlagen.

Резюме — Предлагаются дополнительные критерии для обоснования выбора функции механизма превращения $g(\alpha)$ по методу Шатавы.