

UTILIZATION OF THE AFFINE TRANSFORMATION OF THERMOANALYTICAL CURVES FOR THE DETERMINATION OF KINETIC PARAMETERS

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A method is suggested for the affine transformation of thermoanalytical curves, by means of which their comparison with one another becomes feasible. It is demonstrated that the results obtained by the traditional methods of non-isothermal kinetics depend on the heating rate, whereas the results attained by affine transformation are independent of the heating rate. They are consistent with the results obtained by Merzhanov's dmethod, which is also a non-aprioristic method.

The utilization of thermoanalytical results for the purpose of determining the kinetic parameters of various solid-state reactions has lately become much widespread.

Numerous methods for the kinetic analysis of results achieved in non-isothermal studies have been developed, the most important and largely applied being those cited in references [1–6].

All these methods, however, suffer from several fundamental shortcomings.

First of all, the aprioristic approach to the form of the function $f(\alpha)$ in the basic equation for the rate of reaction

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

frequently results in an arbitrary and physically unfounded character of the function.

The methods suggested for discriminating the mechanism of the reactions by utilizing experimental and theoretical curves [7, 8] do not solve the problem. As we demonstrated in [9], it is impossible to give preference to any one of the possible mechanisms at the error level existing at present in the majority of experimental determinations of process parameters.

Secondly, differing methods of calculation, even at unchanged experimental conditions, may yield non-equivalent values for the kinetic parameters [10].

Thirdly, it has been demonstrated in several research works [11, 12] that at continuous heating at a constant heating rate, the equation of the rate of reaction

must have the form

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t} \right)_T + \left(\frac{\partial \alpha}{\partial T} \right)_t \cdot \Phi \quad (2)$$

where Φ is the heating rate and T the temperature.

Consequently, when using the usual methods of non-isothermal kinetics, a dependence of the calculated process parameters on heating rate should be observed, which has in fact been confirmed experimentally [13].

To eliminate these shortcomings, we suggest in the present paper a novel method: a non-aprioristic description of the kinetics of thermal decomposition at non-isothermal conditions. A similar method proposed by Merzhanov and co-workers [14] is used for comparison. The paper also contains a statistical analysis of the results obtained by various methods.

The model substance used was calcium oxalate monohydrate $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (analytical grade, particle size 0.2 . . . 0.3 mm). To standardize the properties of the samples, crystallization was carried out with natural nucleus formation under standard conditions [15].

The dehydration process was studied with the Derivatograph OD-103 and the scanning microcalorimeter DSM-2.

When using the derivatograph, the thermal dilution method [14] was applied to eliminate the effect of the thermophysical properties of the reacting substance.

Thermal analysis was carried out at different heating rates: 1.25; 2.5; 5.0; 10; 20 $\text{K} \cdot \text{min}^{-1}$ with the Derivatograph and 1.5; 3; 6; 12.5; 25 $\text{K} \cdot \text{min}^{-1}$ with the DSM-2.

In the first stage of our work, we applied the traditional methods of non-isothermal kinetics for the model system:

- (i) the Horowitz–Metzger approach [1];
- (ii) the Coats–Redfern integral method [2];
- (iii) and (iv) two variations of the differential method [3, 16].

Table 1

Kinetic parameters of the dehydration process calculated by various

Heating rate, K/min	Meth-				
	(i)			(ii)	
	E	$\ln Z$	Δ	E	Δ
1.25	159.0	12.9 ± 1.5	0.0–0.8	138.4	0–0.9
2.5	151.5	13.0 ± 2	0.0–0.6	125.5	0–0.9
5.0	146.8	12.2 ± 1.5	0.0–0.9	123.8	0–0.9
10	123.8	9.6 ± 1.0	0–0.65	115.4	0–0.8
20	110.0	8 ± 1	0.07–0.8	107.9	0.3–1

E in $\text{kJ} \cdot \text{mol}^{-1}$

$\ln Z$ in s^{-1}

The results of processing the experimental data obtained with the derivatograph by means of the above-cited methods are listed in Table 1. The statistical analysis of the results was carried out by the methods described earlier [9, 10].

A comparison by the T^2 criterium [9, 10] of the sets of kinetic parameters (E and $\ln Z$) obtained at different heating rates and by different data processing methods demonstrates the absence of sets equivalent to one another. The thermal dilution method applied excludes the effect of the changing thermophysical properties of the substance on the kinetics of the process. Hence the methods utilized do not describe the experiment correctly. The kinetic parameter values obtained by them largely depend on the heating rate, in agreement with the data in the literature [13]. Besides, the values are not equivalent to one another, excluding the possibility of comparing the results obtained with different methods.

In the next stage of our work we utilized methods that do not require an aprioristic knowledge of the form of the function $f(\alpha)$ describing the mechanism of the reaction.

In isothermal kinetics the method of affine transformation of the kinetic curves is widely applied. It allows to make certain conclusions regarding the mechanism of the reaction already in the first stage of the investigation [17]. After some modifications, this method can be applied to thermoanalytical curves under the conditions of linear heating. The axiomatics of this method are similar to the Barret axiomatics [17].

If the configuration of the domain where the chemical stages defining the reaction that takes place on the surface of the solid reactant is identical for some samples and does not depend on temperature, heating rate, partial pressure of the gases evolved, but depends solely on the conversion α , the rate function $v(T, P, \Phi, \alpha)$ can be represented by an expression with separated variables:

$$v(T, P, \Phi, \alpha) = k(T, P, \Phi) \cdot f(\alpha) \quad (3)$$

methods of non-isothermal kinetics. Data obtained with the derivatograph

o d					
(iii)			(iv)		
E	$\ln Z$	Δ	E	$\ln Z$	Δ
133.8	35 ± 6	0.1–0.9	159.9	41 ± 8	0–0.85
125.5	31 ± 4	0.1–0.8	150.6	38 ± 6	0–0.9
117.1	26 ± 1.3	0.1–1	150.6	38 ± 6	0.1–0.9
92.0	22 ± 2.2	0.75	150.6	35 ± 4	0.1–0.85
79.4	16 ± 1.3	0–0.7	125.5	30 ± 7	0.07–0.8

Δ is the linearity range of α

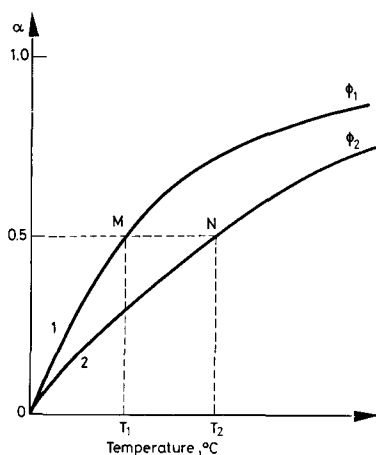


Fig. 1. Affine transformation of curves

where T is temperature, P is pressure, Φ is the heating rate and $f(\alpha)$ the function defining the mechanism. In the range of pressures, temperatures and heating rates where this condition is satisfied, the system will attain one and the same conversion value at different values of any one variable for periods of time differing by a constant factor independent of α . Let us designate two arbitrary curves by 1 and 2 (Fig. 1). Let us assume that these curves were obtained at the heating rates Φ_1 and Φ_2 . Conversion will be identical for both curves in all points where

$$\alpha = \phi(K_1 T_1) = \phi(K_2 T_2) \quad (4)$$

since at constant conversion

$$\Phi = \frac{T - T_0}{t} \quad (5)$$

where T_0 is the temperature at which the transformation starts, and condition (3) will be satisfied at

$$K_1 \Phi_1 t_1 = K_2 \Phi_2 t_2. \quad (6)$$

Consequently, in order to pass from point M on curve 1 to point N on curve 2, time t_1 , and the temperature T_1 corresponding to this time, must be multiplied with the ratio

$$\frac{K_1 \Phi_1}{K_2 \Phi_2} = K_2^1. \quad (7)$$

That is, curve 1 is the affine transformation of curve 2 at a ratio of K_2^1 . Hence, the kinetic curves, plotted in the coordinates

$$\alpha \text{ vs. } \frac{T_i - T_0}{T_\alpha - T_0} \quad (8)$$

will be transformed into one another, if the mechanism of the process does not depend on α and Φ .

The mass change curves obtained at different heating rates were transformed into the new coordinate system (8) by the method described earlier [18]. To confirm the equivalence of the new curves obtained we used the following process.

Table 2

Experimental values of the t -criterion at pairwise comparison of affinely transformed thermoanalytical curves (data obtained with the derivatograph)

Heating rate, K/min	10	5	2.5	1.25
20	0.56	1.52	1.23	1.31
10		1.30	1.48	1.20
5			1.66	0.73
2.5				0.27

For every pair of curves we determined the differences in the ordinates for a certain set of points, and by means of Student's t -criterion we checked the zero-hypothesis on the meaningless difference of the maximum difference of the ordinates from zero, within the reproducibility error of the experiment. The experimental values of the t -criterion are presented in Table 2. For the given number of degrees of freedom, at the theoretical two-directional criterium, we have $t_{0,1} = 1.76$ and $t_{0,05} = 2.15$.

It may be seen from the data in Table 2 that all the curves considered are affinely transformed into one another within the experimental error. To determine the kinetic parameters it is necessary to know the dependence of k in Eq. (3) on temperature. Let us assume that in our case this dependence is the Arrhenius law. It then follows from Eq. (3) that the activation energy can be determined from the slope of the straight line $\log v = f\left(\frac{1}{T}\right)$ plotted for any value of α_2 obtained at different heating rates. After logarithmation of Eq. (6) one obtains

$$\log K_2^1 = \log t_1 + \log \Phi_1 - \log t_2 - \log \Phi_2 = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \quad (9)$$

The activation energy is determined in this case from the slope of $\log t = f(1/T)$, while the free term of the regression equation is the sum

$$\log Z + \log f(\alpha_i) + \log \Phi. \quad (10)$$

Thus the affine transformation represents a transition of the data of the non-isothermal experiment to isothermal conditions. We determined the relationships

$$\log t_{\alpha i} = f\left(\frac{1}{T}\right) \text{ for five heating rates at three fixed conversions } \alpha = 0.1; 0.5 \text{ and } 0.9.$$

In all cases we obtained linear regression equations whose adequateness was confirmed by the method utilized earlier [9, 10]. The data of the calculations are presented in Table 3. The logarithm of the pre-exponential factor is the free term of the regression equation and is determined by Eq. (10). The last two terms of the sum yield a value that is within the experimental error and their effect may be neglected.

In Table 3 we also listed the data obtained with the Merzhanov method [14], also a non-aprioristic method to recalculate the data of non-isothermal experiments into isothermal conditions. These calculations were carried out for one fixed conversion $\alpha = 0.5$ from the thermogravimetric and calorimetric data. The error, as

Table 3

Kinetic parameters of the dehydration process of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, obtained by non-aprioristic processing methods of the thermoanalytical curves

Conversion α	Affine transformation		Merzhanov method			
			Derivatograph		Calorimeter	
	E , kJ/mol	$\ln Z$	E , kJ/mol	$\ln Z$	E , kJ/mol	$\ln Z$
0.1	69.0	15.0 ± 1.6	—	—	—	—
0.5	63.1	14.0 ± 1.3	71.1	16.4 ± 1.5	71.7	16 ± 2
0.9	59.4	13.0 ± 1.1	—	—	—	—

Table 4

Comparison of the evaluation of the dehydration process of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ($T_{\text{theor.}}^2 = 11$)

Method	I: Affine transformation		II: Merzhanov method $\alpha = 0.5$	
	$\alpha_{0.5}$	$\alpha_{0.9}$	Derivat.	Calorimeter
I $\left\{ \begin{array}{l} \alpha = 0.1 \\ \alpha = 0.5 \\ \alpha = 0.9 \end{array} \right.$	8.7	9.5 4.7	6.2 10.0 18	5.5 10.0 20
II Derivatograph $\alpha = 0.5$				0.5

may be seen from the table, is substantially larger than with our method. This is because with the Merzhanov method, the thermogravimetric curves must be graphically derived and the results of the calorimetric experiment must be graphically integrated.

A comparison of the sets of kinetic parameters obtained with both methods (within each method and with one another) utilizing the Hottelling T^2 -criterion demonstrated the equivalentness of the results in almost all cases (Table 4).

In conclusion, the presented material demonstrates that the non-aprioristic methods yield agreeing and consistent results. The method of affine transformation demonstrates that changes in the heating rate do not affect the mechanism of the process. The temperature dependence of the rate of reaction is identical in all cases and does not depend on conversion. Consequently, the method suggested for the comparison of thermoanalytical curves and for the determination of the kinetic parameters has substantial advantages as compared to the traditionally used methods on non-isothermal kinetics.

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RÉSUMÉ — On propose une méthode pour la transformation affine des courbes d'analyse thermique, qui permet leur comparaison. On montre que les résultats obtenus par les méthodes traditionnelles de cinétique non-isotherme dépendent de la vitesse du chauffage, tandis que les résultats obtenus par la transformation affine n'en dépendent pas. Ils sont en accord avec les résultats de la méthode de Merzhanov.

ZUSAMMENFASSUNG — Eine Methode zur Affintransformierung thermoanalytischer Kurven wird vorgeschlagen, wodurch ihr Vergleich miteinander ermöglicht wird. Es wird gezeigt, daß die durch traditionelle Methoden der nicht-isothermen Kinetik erhaltenen Ergebnisse von der Aufheizgeschwindigkeit abhängig sind, während die durch Affintransformierung erhaltenen von der Aufheizgeschwindigkeit unabhängig sind. Sie sind in Übereinstimmung mit den nach der Methode von Merzhanov erhaltenen Ergebnissen, die ebenfalls eine nicht-aprioristische Methode ist.

Резюме — Предложен метод преобразования термоаналитических кривых, посредством которого становится возможным сравнение их друг с другом. Показано, что результаты, полученные традиционными методами неизотермической кинетики, зависят от скорости нагрева, тогда как результаты, полученные на основе предложенного преобразования, не зависят от скорости нагрева. Результаты совпадают с результатами, полученными по методу Мержанова, являющимся также неаприорным методом.