

A STATISTICAL COMPARISON OF NON-ISOTHERMAL METHODS OF KINETIC INVESTIGATION

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A statistical analysis of some non-isothermal kinetic techniques is given. Comparison of the kinetic parameter values obtained by different techniques has shown them to be statistically non-equivalent. Hypotheses of significance or non-significance of discrepancies in the kinetic parameter values should therefore be tested using two-dimensional normal distributions. Comparisons of the results obtained by various techniques using activation energy values only lead to erroneous conclusions.

During recent years, the method of thermogravimetric measurements under conditions of uniformly increasing temperature has been widely applied to study the kinetics of thermal decomposition of solids. A number of techniques have been suggested for calculation of kinetic parameters from data obtained with a derivatograph. A detailed review of most non-isothermal methods of kinetic investigations is given in the works [1, 2]. Šestak *et al.* [2] have made an attempt to analyze their accuracy and effects on kinetic parameter values, to show that the results obtained using various techniques differ by not more than 10%, and all techniques may be used in calculations of kinetic parameters. In our view, however, the procedure applied to compare the calculation techniques is not quite a correct one, in particular because of the neglect of measurement errors. No criteria for a choice between the calculation techniques used in the processing of non-isothermal data has been suggested as yet, except in the work by Merzhanov [4]. Even that work, however, contains no statistical analysis. Most authors imply that various techniques should lead to equivalent results, and then only on the grounds that the various non-isothermal data-processing methods are derived from one and the same equation:

$$\frac{d\alpha}{f(\alpha)} = Zq \exp\left(-\frac{E_a}{RT}\right) dT \quad (1)$$

where α is the extent of conversion, Z the Arrhenius pre-exponential factor, q the rate of temperature increase, E_a the activation energy, T the temperature, and $f(\alpha)$ a function depending on the reaction mechanism. Integration of (1), however, is a difficult task. In fact, the analytical expression for $f(\alpha)$ is usually not known* as

* Most frequently, $f(\alpha)$ is written in the form $d\alpha/dt = k(1 - \alpha)^n$.

the function depends on the reaction mechanism, which is often unknown as well; next, the right-hand side of (1) can not be integrated explicitly; lastly, (1) is only valid if the temperature dependence of the rate constant follows the Arrhenius equation. Hence, the differences in the results may depend not only on the integration technique chosen, but also on the approximations used to overcome the difficulties specified. The methods of integration of the right-hand side of Eq. (1) may be divided into four groups [1]: (i) approximative methods, (ii) integral methods, (iii) differential methods, (iv) methods based on temperature maxima shifts.

In this work, we give a statistical analysis of some non-isothermal kinetic techniques. The results obtained under isothermal conditions are used as reference. The latter may seem unjustified [5]. However, if the reaction starts simultaneously at all sample surface points, the results obtained under isothermal and polythermal conditions should be identical, provided the boundary surface between the phases is produced prior to the experiment. This may be done by generating nucleation centres under standard conditions [6].

Four non-isothermal kinetic techniques used most frequently have been compared. The first one is the Horowitz–Metzger approximative method [7]. The calculations were made using the equation

$$\ln[1 - (1 - \alpha)^{1-n}] = \ln(1 - n) + (E/RT_{\max}^2)\Theta \quad (3)$$

$$\text{where } \Theta = T_{\max} - T_i;$$

$$\text{with } n = 1,$$

$$\ln \ln(1 - \alpha) = (RT_{\max}^2/E)\Theta. \quad (4)$$

The second method is the integral method suggested by Coates and Redfern [8].

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right] = \ln \frac{ZR}{qE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{RT} \quad (5)$$

and, with $n = 1$

$$\ln \left[-\ln \frac{(1 - \alpha)}{T^2} \right] = \ln \frac{ZR}{qE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{RT}. \quad (6)$$

The third and the fourth techniques tested are the versions of the differential method suggested by Zhabarova and Shkarin [9, 10]:

$$\ln \left[\frac{1}{(1 - \alpha)^n} \frac{d\alpha}{dT} \right] = \ln \frac{Z}{q} - \frac{E}{RT} \quad (7)$$

and, with $f(\alpha)$, the Erofeev–Avraami equation:

$$\ln \left[\frac{\alpha^n(1 - \alpha)}{1} \frac{d\alpha}{dT} \right] = \ln \frac{Z}{q} - \frac{E}{RT}. \quad (8)$$

It should be noted that the quantity n in (8) has a different physical sense from that in all the other equations, where it stands for the effective reaction order. In this work, these quantities are only treated as certain constants, irrespective of their physical meaning, and for this reason the same notations are used in all the equations. All the methods specified were applied to determine the kinetic parameters from data obtained by means of a derivatograph.

Experimental

The comparative analysis of the data-processing methods was performed using calcium oxalate hydrate dehydration as example. The compound was of 'pure for analysis' grade, 0.025–0.010 mm fraction. Measurements were made on an OD-102 derivatograph, at a 5°/min temperature increase rate, with weighed samples of ca. 30 mg.

The isothermal experiments were carried out with a TGS-1 Perkin–Elmer set for six temperatures in the range 150–250°. The activation energy of the isothermal process was determined using the spontaneous nucleation technique under standard conditions [6]. The estimates for kinetic parameters obtained from isothermal experiments were as follows: activation energy, E_a , 21 ± 1.5 kcal/mole, logarithm of the pre-exponential factor of the Arrhenius equation, $\ln Z$, 22 ± 2 .

Results and discussion

All the equations under consideration, (3–8), may be linearized by respective substitutions of variables at certain n values. To calculate the kinetic parameter values corresponding to a given data-processing method, the n value (or a range of n values) should first of all be determined which makes the linearization possible:

$$y = a + bx \quad (9)$$

where a and b are proportional to the kinetic values. The calculations were performed with the following n values: 0, 1/3, and 3/4 for the first, second and third methods, and 1/2, 1, 2, 3 and 4 for the fourth method. The n values with which the transformed equations are linearly adequate are listed in Tables 1 and 2.

A special statistical test for linearity was applied [11] to ensure the detection of even minor deviations from linearity. The basic idea of the test is statistical comparison of two linear regression equations constructed for adjacent regions. If the equations are non-equivalent statistically, deviation from linearity in a wider region comprising the two initial ones is of significance. If, on the contrary, no break occurs, the region is extended to include both initial regions, a new regression equation is then determined and compared with a regression equation for an adjacent region, and so on. Statistical equivalence of two equations is tested by comparison first of straight line slopes, and then, if these are identical, of their free terms.

Table 1
Kinetic parameters for dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

Technique		E , kcal/mole	$\ln Z$	Linearity interval
I. Horowitz— Metzger approximative technique	2/3	23.1 ± 0.7	25 ± 3	0.05 — 0.65
	3/4	22.8 ± 0.7	24 ± 3	0.05 — 0.70
	1	22.3 ± 0.6	23 ± 3	0.05 — 0.89
II. Coates— Redfern integral technique	2/3	20.9 ± 0.5	43 ± 5	0.04 — 0.87
	3/4	21.3 ± 0.5	44 ± 5	0.04 — 0.90
	1	18.9 ± 0.5	45 ± 5	0.05 — 0.75
III. Differential technique	2/3	15 ± 1	14 ± 1.5	0.05 — 0.75
	3/4	16 ± 1	15 ± 1.5	0.05 — 0.75
	1	19 ± 1.5	19 ± 2	0.1 — 0.75
IV. Isothermal method	—	21.5 ± 1.5	22 ± 2	—

Simultaneously, the kinetic parameter values were estimated using the non-isothermal techniques chosen (Table 1). One may see that various techniques provide an adequate description of the experimental data with n values in certain ranges rather than with definite n values. All techniques employing Eq. (6) give the same range of n values, though linearity intervals and kinetic parameter values differ somewhat.

Table 2
Comparison of kinetic parameter estimates for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ dehydration
(T_{their}^2 test value of ca. 4)

Method	I		II			III		IV				Isothermal method								
	2/3	3/4	1	2/3	3/4	2/3	3/4	1	2	3	4									
I	2/3	2.5	14	50	720	50	45	17	56	2.5	12	15								
	3/4		3	800	200	50	60	17	72	10	20	20								
	1		750	700	40	30	7.0	250	25	25	2.5									
II	2/3				3.5	1500	1100	900	500	200	140	100								
	3/4					1300	1200	1000	550	240	180	150								
	1						1.0	17	63	60	50	50								
III	2/3																			
	3/4																			
	1																			
IV	2																			
	3																			
	4																			

I — the Horowitz— Metzger approximative method

II — the integral method

III— IV — the differential methods

It thus appears that measurement errors are responsible for the appearance of certain ranges of n values where the equations provide adequate descriptions of the experimental data.

Further, a statistical comparison of the kinetic parameter values was carried out. It should be borne in mind that the parameters a and b in (9) correlate with each other. The correlation coefficients were determined to be as a rule 0.9. Hypotheses of significance *vs.* non-significance of discrepancies in the kinetic parameter values should therefore be tested using two-dimensional normal distributions, rather than by comparing the values for a given parameter separately, as is done only too often. The Hotelling T^2 -test [12] was applied to compare general means of two data series from abnormally distributed sets. The T^2 -test value was calculated by the equation:

$$T^2 = \frac{1}{2(1 - r^2)} \left[\left(\frac{d_1}{Sa_1} \right)^2 + \left(\frac{d_2}{Sa_2} \right)^2 - 2r \frac{d_1}{Sa_1} \cdot \frac{d_2}{Sa_2} \right] \quad (9)$$

where $d_1 = a_1 - a_2$ and $d_2 = b_1 - b_2$; a and b are the regression equation parameters, and r is the correlation coefficient. The hypothesis of deviation significance was accepted or discarded after comparison of the theoretical and experimental T^2 values. Table 2 summarizes T^2 values obtained by comparison of the kinetic parameters both within a series of the values calculated by the same technique, and between series of data obtained by various techniques. Comparison of the results of isothermal experiments was also made. As expected, the kinetic parameters for various n within series of data obtained by each data-processing technique are statistically equivalent. Comparison of the kinetic parameter values obtained by different techniques shows them to be statistically non-equivalent.

Comparison of the non-isothermal and isothermal data reveals that only the Horowitz–Metzger technique with $n = 1$ and the third (differential) method give kinetic parameter values similar to those determined from the isothermal experiment.

It thus follows that the non-isothermal kinetic techniques compared give non-equivalent kinetic parameter values, which is contrary to what is generally assumed. The results obtained by these and like methods should therefore be used only cautiously, especially when comparing the results obtained under different assumptions. Comparisons of the results obtained by various techniques using activation energy values only, as e.g. in [13], are not justified and lead to erroneous conclusions. It should be noted that n variations within certain limits do not affect the kinetic parameter values. The scatter of n frequently observed in studies of thermal decomposition reactions (see e.g. [14]) is, apparently, not inherent in their specific physicochemical features. Rather, it depends on the variance of reproducibility of the experimental results.

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ZUSAMMENFASSUNG — Es wird eine statistische Analyse einiger nicht-isothermer kinetischer Techniken gegeben. Der Vergleich der durch verschiedene Methoden erhaltenen Werte der kinetischen Parameter zeigte, dass diese statistisch nicht äquivalent sind. Die Hypothesen der Signifikanz oder Nichtsignifikanz der Diskrepanzen der Werte der kinetischen Parameter sollten deshalb eher unter Anwendung zweidimensionaler Normalverteilungen als durch Vergleich der für einen gegebenen Parameter erhaltenen Werte geprüft werden.

Резюме — Дан статистический анализ некоторых методов неизотермической кинетики. Сравнение величин кинетических параметров, полученных различными методами, показало, что эти методы дают неэквивалентные результаты. Гипотеза о значимости или незначимости различий в наборах кинетических параметров должна проверяться с использованием двумерного нормального распределения. Сравнение отдельных кинетических параметров между собой приводим к ошибочным выводам.