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STATISTICAL ANALYSIS OF THERMOANALYTICAL EXPERIMENTAL DATA

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Abstract

A statistical technique based on the Wilcockson criterion is suggested for estimation of the reproducibility of thermoanalytical experiments. Reduction of the whole physicochemical process to a quasi-one-stage process is described.

Keywords: kinetics, statistical analysis

Introduction

In thermoanalytical experiments, non-isothermal kinetic techniques are extensively used to study mechanisms of heterogeneous processes [1].

Thermoanalytical data are interpreted in terms of formal kinetics, which requires estimating the parameters of mathematic models, on which the formal kinetic theory of chemical reactions is based. This is done by solving the inverse kinetic problem. However, as a rule, a solution to the inverse kinetic problem is difficult to obtain, because non-isothermal chemical reactions are combinations of various physicochemical processes, such as chemical conversion, diffusion, nucleation, etc. The description of the whole set of processes by means of formal kinetics appears to be impossible.

It is, however, possible to find such experimental conditions under which the rate-determining stage (the slowest stage) will be chemical conversion, which is most difficult to model. Such processes are called quasi-one-stage processes.

The problem of comparing experimental data without solving the inverse kinetic problem arises when experimental conditions change. When experiments are performed under isothermal conditions, the affine transform [2] is successfully used. For non-isothermal TA-curves, the affine transform is only applicable when the reaction rate is independent of conversion, i.e. when the reaction is a zero order process. In practice, this happens fairly rarely. This prompted us to

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elaborate special statistical techniques for testing the significance of discrepancies between experiments.

This paper deals with application of statistical methods to thermoanalytical experiments for estimating the influence of different experimental conditions on the properties of substances.

Experimental

The thermal dehydration of lithium sulphate monohydrate $Li_2SO_4{\cdot}H_2O$ was studied. This reaction is considered a quasi-one-stage process [3]. The starting material was polycrystalline $Li_2SO_4{\cdot}H_2O$ (analytical grade) recrystallized from a saturated aqueous solution at room temperature. Several groups of samples were prepared. The first group included $Li_2SO_4{\cdot}H_2O$ polycrystals ground in a ball mill. Samples of the second group had narrow particle size distribution and were prepared by grading samples of the first group on sieves with different cell sizes. This group was divided in two subgroups, containing small (0.032–0.045 mm) and middle-size (0.045–0.063 mm) particles. The third group included homogeneous samples of middle-size particles preliminarily partially (by ≈10%) dehydrated, as occurs in the course of natural nucleation under standard conditions [4]. The procedure for preparing these samples was as follows.

$Li_2SO_4{\cdot}H_2O$ powder from the second group of samples was held in a thermostat at a fixed temperature (as high as is necessary to initiate dehydration) until 10–12% of water was lost. Each group included 5–7 samples, which were studied in static air atmosphere (SAA) and in dynamic inert atmosphere of dry nitrogen or argon (DIA). Several experiments were performed under vacuum.

As usual, we performed two groups of experiments: a series of parallel experiments to characterize reproducibility and experiments at various heating rates.

All experiments were performed on a TGA-7 Perkin-Elmer thermogravimetric instrument. We used a thin cylindrical sample holder made of platinum. Sample weights were about 3 mg. Gas flow rates of 60 ml min^{-1} were used in DIA experiments.

Results and discussion

SAA experiments on samples of the first and second groups demonstrated that the decomposition of $Li_2SO_4{\cdot}H_2O$ has a complex nature, i.e. is not a quasi-one-stage process. This follows from the shapes of the curves of the first and second conversion derivatives. The experimental curves and curves modelling a quasi-one-stage process are shown in Figs 1 and 2. The specific 'bulge' of the curve shown in Fig. 1 and the split minimum of the curve shown in Fig. 2 indicate the existence of two or more parallel processes with maximum rates at slightly different temperatures. All of them significantly influence the rate of the overall process.

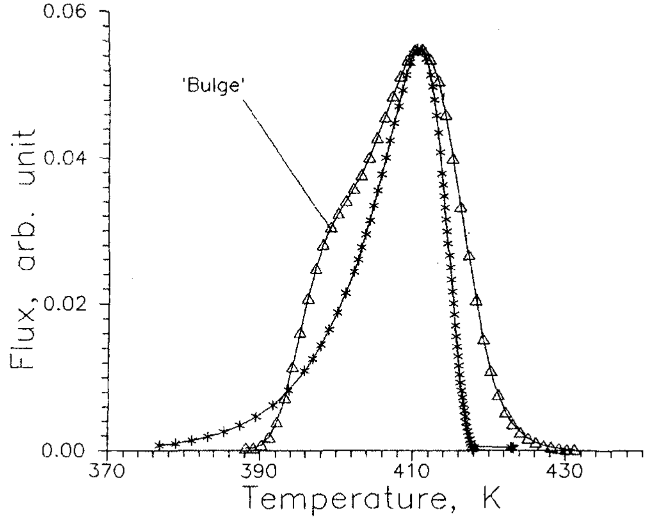

Fig. 1 Comparison of model and experimental curves using $d\alpha/dT$ values. Δ – experimental curve, * – quasi-one-stage model curve

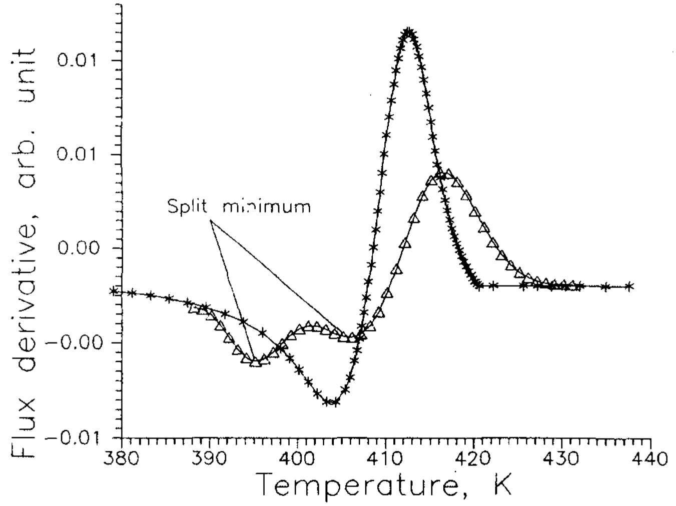

Fig. 2 Comparison of model and experimental curves using $d^2\alpha/dT^2$ values. Δ – experimental curve, * – quasi-one-stage model curve

Experiments with monodisperse samples performed under vacuum and in DIA give virtually the same results. On the other hand, samples subjected to natural nucleation show a significantly different behaviour (Fig. 3). This means that nucleation significantly affects the kinetics of dehydration, which explains the polymodal character of experimental curves. This is the reason why experi-

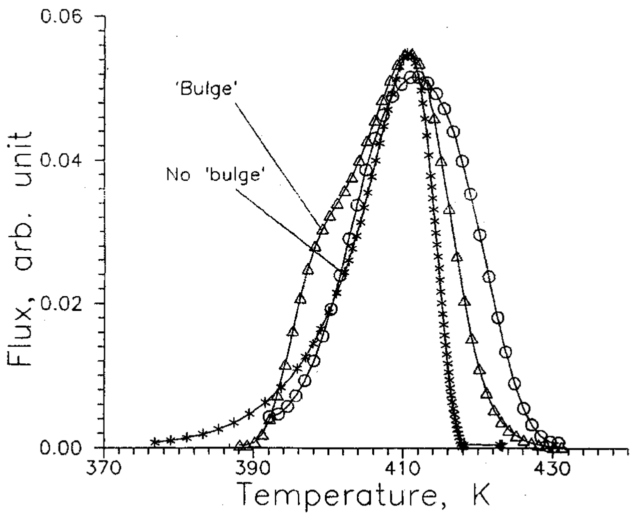

Fig. 3 Results of experiments on samples subjected to natural nucleation. o – experiment with preliminary nucleation, Δ – experiment without preliminary nucleation, * – quasi-one-stage model curve

ments performed in a dynamic atmosphere on samples with a unified surface formed under natural nucleation conditions show a behaviour closest to that characteristic of quasi-one-stage processes.

To determine the reproducibility conditions we performed a series of parallel quasi-one-stage dehydration experiments at 10 K min^{-1} heating rate. At the first stage of reproducibility estimation, the curves should be tested for the presence of irregular spikes. This is done by pairwise comparison of all the curves to reveal the influence of the experimental conditions on curve shapes. In other words the influence of treatment should be studied.

This cannot be done using common statistical methods because, as a rule, the distribution of deviations for experimental points is unknown, and the elements of an experimental sample can hardly be considered independent random values.

This requires use of non-parametric techniques for comparing different samples. Non-parametric techniques do not consider means and variances (i.e. 'parameters'). Such methods work without information about the distribution function and the asymptotic behaviour of this function. Neither does it make difference whether or not sample elements are statistically independent. It is only necessary that the samples under comparison should be independent of each other.

As far as we can judge, such a comparison can best be done using the Wilcockson statistics and criterion [5, 6]. We employed this criterion to estimate the influence of treatment on thermoanalytical data. The characteristics of non-parametric techniques are also inherent in the Wilcockson criterion. This means that systematic shifts caused by equipment-sample response and the Arrhenius relation between the reaction rate and temperature pose no difficulties for testing the null hypothesis using the specified criterion. Although this criterion is described in detail in the literature, it is worth while describing it here briefly in order to illustrate the application of the Wilcockson criterion to thermoanalytical data.

Two samples $x_1,...,x_m$ and $y_1,...,y_n$ of sizes m and n are analysed. The elements of the samples can be $\alpha_i(T)$ or $d\alpha_i(T_j)/dT_j$, where a_i are the conversions in sample i, i=1,2, $d\alpha_i(T_j)/dT_j$ are the first derivatives of the conversions with respect to temperature, T_j are the temperatures at which the α_i values were obtained, $j>10$. We recommend to use the first derivative values, which show the differences between experiments and reaction mechanisms most clearly. Sample distributions $F(x)$ and $F(y)$ or retrievals should be continuous and the samples should be independent of each other.

The hypothesis H_o: $F(x)=F(y)$ of homogeneity of the samples is tested. The elements of the samples should be arranged into a variation row in the ascending order, for example $y_1x_1y_2y_3x_2y_4x_3x_4y_5...x_my_n$. Ranks of '$y$' are calculated for the summed sample. Let us denote ranks of 'y' as $S_1,...,S_n$. Now it is possible to calculate the Wilcockson statistics $W=S_1+...S_n$. It is known [5, 6] that if $m>10$ and $n>2$, W is distributed normally with the parameters $M_w=mn/2$ and $D_w= mn(m+n-1)/12$. For large samples we can therefore use normal distribution to calculate confidence intervals for various confidence levels. In all our calculations we used a confidence level of 0.05. This gives the following rule for testing the null hypothesis H_o:

H_o should be rejected at a confidence level of 0.05 if

$$[M_w - W] \geq 1.98 \cdot \sqrt{D_w}$$

The Wilcockson criterion cannot only be successfully used to test the identity of process mechanisms for series of parallel experiments at the same heating rate, but can also be applied to experiments performed under different conditions, for example in different atmospheres, at various heating rates, etc. This makes this criterion extremely valuable, because a reliable solution of the inverse kinetic problem can be obtained by only evaluating experiments at various heating rates [7].

Statistical analysis of thermoanalytical data obtained under different conditions was performed as follows.

The most probable values of formal kinetic model parameters were estimated from the data of parallel experiments. Curve fitting was performed by a non-linear least squares procedure. The parameter values are the more reliable the larger the number of reproducibility experiments. The principal formal kinetic model

$$\frac{d\alpha}{dT} = \frac{k_o}{\beta} \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \tag{1}$$

was used as the mathematical model of the process. Here α is the conversion, T is the temperature, k_0 is the pre-exponential factor, β is the heating rate, E_a is the temperature coefficient of the reaction rate (activation energy), R is the gas constant, and n is the reaction order.

We used model (1) as an interpolating function to approximate the experiments at various heating rates β. We took into account that the formal kinetic parameters have no physical meaning, they are used only to approximate and model the process under different experimental conditions, not to interpret the mechanisms of physicochemical processes.

Average parameter values obtained for parallel experiments can be used for modelling experiments at various heating rates. As was mentioned, the technique of joint treatment of experiments performed at various heating rates helps to reduce uncertainties involved in kinetic parameter values.

The experimental curves obtained at various heating rates can seemingly be compared, because the Wilcockson criterion offers such a possibility. The Wilcockson criterion is, however, a mathematical criterion and can only be used to compare samples rather than reaction mechanisms. Before comparing, experiments should therefore be adjusted to the same 'scale', that is to the same heating rate. If we have (even formal) parameter values determined at one heating rate, we can model the behavior of the substance at another heating rate. This model experiment would contain information about the same mechanism of the same process, but carried out at a different heating rate. Let us assume that we also performed a real experiment at the heating rate of the model experiment. A comparison of real and model experiments performed at the same heating rates thus reduces to a comparison of two reproducibility experiments. So, the absence of reproducibility in such conditions means that there is a significant difference not only between two statistical samples, but also reaction mechanisms.

Table 1 illustrates the results of comparison of two samples. The samples were obtained in experiments performed in SAA on a substance subjected to natural nucleation at various heating rates. It is obvious that mechanisms of

Table 1 Statistical comparison of experiments performed in SAA at various heating rates. The basic experiment is 10 K min^{-1}

Pares	β/K min^{-1}	W	M	S	M–σ – M+σ	Conclusion
1–1′	1	1436	1058	127	807–1309	different
2–2′	2.5	1937	1741	184	1376–2105	same
3–3′	5	1689	1568	170	1231–1905	same
4–4′*	10	1456	1405	157	1094–1715	same
5–5′	20	1734	1513	166	1184–1841	same
6–6′	30	1858	1568	170	1231–1905	same
7–7′	50	1646	1301	148	1008–1594	different

processes at high (50 K min^{-1}) and at low (1 K min^{-1}) heating rates differ from the mechanism of the same process at 10 K min^{-1}. The basic experiments for parameter estimation can be different. The same comparison shows that the mechanism of the studied process is in continuous dependence on the heating rate. The experiment chosen as the basis for parameter estimation in the table was marked '*'. Numbers of experiments are given in accordance with their heating rates in ascending order. Label ''' indicates that this experiment is model. Each pair thus consists of a real and a model experiment. Other symbols are the following: β is the heating rate, W is the number of inversions, M is the mean of inversions, S is the standard deviation of inversions, σ is the confidence interval, 'conclusion' is the conclusion about the identity of mechanism in experiments compared by pairs.

The experimental results obtained in a dynamic atmosphere were used to solve the inverse kinetic problem according to the technique described in [7]. The formal kinetic model

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{k_o}{\beta}\exp\left(-\frac{E_a}{RT}\right)\alpha^m(1-\alpha)^n \tag{2}$$

was used. The parameters are: α is the conversion, T is the temperature, k_o is the pre-experimental factor, β is the heating rate, E_a is the temperature coefficient of reaction rate (activation energy), R is the gas constant, n and m are the reaction orders.

Natural nucleation under standard conditions results in such a mechanism that the reaction rate is limited by the velocity of reaction surface movement, so 'm' in Eq. (2) should be zero.

Combined treatment of three experiments realizing this mechanism gives the following set of parameters: $\mathrm{Ln}(k_o)=19.9$ (8.0), $E_a/R=10554$ (3400) K, $n=0.66$ (0.4), $m=0$, cond=66, where 'cond' is the condition number of the kinetic problem. The errors estimated by the Monte-Carlo method are given in parentheses.

Final verification of the parameters obtained by solving the inverse kinetic problem requires numerical integration of Eq. (2), which is the direct kinetic problem.

The calculated curves, were compared with experimental curves using the variance ratio

$$\frac{S^2_{\mathrm{exp}}}{S^2_{\mathrm{theor}}} \tag{3}$$

where S^2_{exp}, is the variance of reproducibility of experimental data and S^2_{theor}, is the joint variance of the differences between calculated and experimental values. In the performed experiments the values of (3) are 0.4 (for 2.5 K min^{-1}), 0.27 (for 5 K min^{-1}) and 0.15 (for 20 K min^{-1}). This means that the direct solution of

Eq. (2) with the parameters given above is adequate to experiment and the reaction mechanism does not change in the 2.5–20 K min^{-1} range of heating rates.

The same technique was applied to experimental data obtained in static atmosphere in the same range of heating rates. The results were as follows: $\text{Ln}(k_0)=23.3$ (9.8), $E_a/R=12200$ (4140) K, $n=0.44$, cond=105. The variance ratio values: 32.7 (for 2.5 K min^{-1}), 9.1 (for 5 K min^{-1}) and 0.5 (for 20 K min^{-1}). These results prove that the solution obtained does not describe experimental data and that the mechanism significantly changes from one heating rate to another.

So, two different methods that we used in our work gave the same conclusion about the process studied under different conditions.

Conclusion

In this paper we suggest a statistical technique based on the Wilcockson criterion and non-linear LSM for comparison and evaluation of thermoanalytical experimental data. An original software package realizing this technique was elaborated in order to simplify the described operations with experimental data. This software package makes it possible to give reliable conclusions about the mechanisms of the studied processes and their changes depending on experimental conditions quickly and efficiently.

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