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A kinetic study of the thermal decomposition process of potassium metabisulfite: Estimation of distributed reactivity model

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Abstract

The thermal decomposition kinetics of potassium metabisulfite was studied by thermogravimetric (TG) and differential thermogravimetric (DTG) techniques using non-isothermal experiments. The apparent activation energy (E_a) is determined using the differential (Friedman) isoconversional method. The results of the Friedman's isoconversional analysis of the TG data suggests that the investigated decomposition process follows a single-step reaction and the observed apparent activation energy was determined as $122.4 \pm 2.1\,\mathrm{kJ\,mol^{-1}}$. A kinetic rate equation was derived for the decomposition process of potassium metabisulfite with contracting area model, $f(\alpha) = 2(1-\alpha)^{1/2}$, which is established using the Malek's kinetic procedure. The value of pre-exponential factor (A) is also evaluated and was found to be $A = 1.37 \times 10^{12}\,\mathrm{min^{-1}}$. By applying the Miura's procedure the distributed reactivity model (DRM) for investigated decomposition process was established. From the dependence α versus E_a, the experimental distribution curve of apparent activation energies, $f(E_a)$, was estimated. By applying the non-linear least-squares analysis, it was found that the Gaussian distribution model (with distribution parameters $E_0 = 121.3\,\mathrm{kJ\,mol^{-1}}$ and $\sigma = 1.5\,\mathrm{kJ\,mol^{-1}}$) represents the best reactivity model for describing the investigated process. Using the Miura's method, the A values were estimated at five different heating rates and the average A values are plotted against E_a. The linear relationship between the A and E_a values was established (compensation effect). Also, it was concluded that the E_a values calculated by the Friedman's method and estimated distribution curve, $f(E_a)$, are correct even in the case when the investigated decomposition process occurs through the single-step reaction mechanism.

Keywords: A. Inorganic compounds; C. Thermogravimetric analysis (TGA); D. Surface properties

1. Introduction

Potassium metabisulfite, $K_2S_2O_5$, is a white crystalline powder with a pungent sulfur odor. $K_2S_2O_5$ is also chemically very similar to sodium metabisulfite [1]. Even at room temperature it deliberates gaseous sulfur dioxide (SO_2) thus acting as a potent antioxidant, protecting both the color, and delicate flavors of wine [1], and may be used as the activator in the particular polymerization processes [2,3].

The decomposition may be described by the following chemical equation:

$$K_2S_2O_{5(s)} \rightarrow K_2O_{(s)} + 2SO_{2(g)} \uparrow, \quad (1)$$

where the potassium monoxide (K_2O) is a solid salt, whereas the SO_2 is a gas. Malanchuk investigated experimentally the decomposition of sodium metabisulfite [4]. It was found that the thermal decomposition of sodium metabisulfite in air atmosphere involves two major weight changes before the final formation of sodium sulfate. The first presented an endothermic process, in which SO_2 is evolved, leaving a residue of sodium sulfite. The second change leads to the formation of sodium sulfate by oxidation of the sulfite [4]. There are, however, the intermediate decomposition reactions, occurring at the second change, which lead to the formation of elemental sulfur and to incomplete recovery of the original sulfur in the final sulfate product [4]. Bogushevich et al. [5] analyzed the nature of thermally induced ion-radicals appearing in $K_2S_2O_5$ subjected to X-ray irradiation. In addition,

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$K_2S_2O_5$ was used for the electron spin resonance study of the sulfur dioxide radical anion ($SO_2^{\bullet -}$) [6].

From the literature survey, it was concluded that the thermal decompositions of metabisulfites are studied very scarcely. The present authors are given a first complete kinetic analysis (determination of full kinetic triplet (Arrhenius parameters (A and E_a) and reaction model function, $f(\alpha)$)) of the thermal decomposition of $K_2S_2O_5$ by the following presented methods: (a) differential isoconversional (model-free) method [7] and (b) Málek's kinetic procedure [8–10]. Also, in this paper, the distributed reactivity model (DRM) for investigated decomposition process was established. For estimating the DRM for considered process, the Miura's procedure [11,12] was used.

2. Experimental

Thermal decomposition of $K_2S_2O_5$ (Merck, 99.5%, powder) was studied by thermogravimetry using a TA SDT 2960 thermobalance, enabling simultaneous recording of TGA and DTA curves. The average mass of samples was about 15 ± 1 mg. Purging gas was nitrogen (99.9995 vol%) at a flowing rate of $90\,\mathrm{mL\,min^{-1}}$. The furnace temperature rose linearly at heating rates: 2.5, 5, 10, 15 and $30\,^{\circ}\mathrm{C\,min^{-1}}$, in the temperature range from an ambient one up to 600 °C.

The original mass loss versus temperature (TG) curves obtained at constant heating rate were transformed into the degree of conversion (α) versus temperature curves by means of the following equation:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}, \tag{2}$$

where m_t represents the mass of the sample at arbitrary time t (or temperature T), whereas m_0 and m_f are the mass of the sample at the beginning and at the end of the process, respectively.

3. Kinetic study

The governing equation for kinetic analysis of solid-state decomposition can be expressed as

$$\frac{d\alpha}{dt} = k(T) f(\alpha), \tag{3}$$

where t is the time, $k(T)$ the temperature-dependent rate constant and $f(\alpha)$ represents the differential conversion function (reaction model). The reaction models may take various analytical forms and some of them used in this work are listed in Table 1.

The explicit temperature dependence of the rate constant is introduced by replacing $k(T)$ with the Arrhenius equation, which gives

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha), \tag{4}$$

where A is the pre-exponential (frequency) factor, E_a is the apparent activation energy and R is the gas constant. In the case of a non-isothermal reaction, the applied heating rates are constant and the temperature can be expressed as $T = T_0 + \beta t$ (T_0 is the initial temperature) in which the constant heating rate, β, is given as $dT/dt = \beta$. Using this transformation, Eq. (4) can be converted into

$$\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha). \tag{5}$$

The use of Eq. (5) supposes that a kinetic triplet ($A, E_a, f(\alpha)$) describes the time evolution of a physical or chemical change.

Table 1
The basic kinetic models and properties of $y(\alpha)$ and $z(\alpha)$ functions

Kinetic models	Symbol	$f(\alpha)$	$g(\alpha)$	$y(\alpha)$	$z(\alpha)$
Johnson–Mehl–Avrami	JMA(n)	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	$[-\ln(1-\alpha)^{1/n}]$	Concave for $n<1$, linear for $n = 1$, maximum for $n>1$	0.632
Phase-boundary controlled reaction (contracting area, i.e., bidimensional shape or one-half order kinetics)	R2, F1/2	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$	Convex	0.750
Phase-boundary controlled reaction (contracting volume, i.e., tridimensional shape or two-thirds order kinetics)	R3, F2/3	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$	Convex	0.704
Two-dimensional diffusion (bidimensional particle shape) Valensi equation	D2	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha)+\alpha$	Concave	0.834
Three-dimensional diffusion (tridimensional particle shape) Jander equation	D3	$3(1-\alpha)^{1/3}/2[(1-\alpha)^{-1/3}-1]$	$[1-(1-\alpha)^{1/3}]^2$	Concave	0.704
Three-dimensional diffusion (tridimensional particle shape) Ginstling–Brounshtein	D4	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	Concave	0.776

Upon integration Eq. (5) gives

$$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E_a}{RT}\right)\mathrm{d}T \approx\frac{A}{\beta}\int_0^{T}\exp\left(-\frac{E_a}{RT}\right)\mathrm{d}T =\frac{AE_a}{R\beta}\int_0^{x}\frac{\exp(-x)}{x^2}\,\mathrm{d}x=\frac{AE_a}{R\beta}p(x), \tag{6}$$

where $g(\alpha)$ is the integral form of the reaction model and $p(x)$ is the temperature integral, for $x=E_a/RT$, which does not have analytical solution. To overcome this difficulty, the temperature integral has been solved using approximation methods, series, expansions, and numerical solution methods [13]. If T_0 is low, it may be reasonably assumed that $T_0\to 0$, so that the lower limit of the integral on the right-hand side of Eq. (6), T_0, can be approximated to be zero.

3.1. Apparent activation energy estimation

3.1.1. Isoconversional (model-free) method

The aim of the kinetic analysis of solid-state reactions is the selection of the $f(\alpha)$ and $g(\alpha)$ functions, which give the best approximation of experimental data. The disadvantage that the several kinetic models provide a similar description of the studied processes is caused by the strong interrelation between the used kinetic functions [14,15]. Often the choice of an appropriate model based on additional information, e.g., morphological studies, is hampered by the discrepancies between the real process and idealized models.

The model-independent (model-free) kinetic analysis, on the other hand, leads to an estimation of the apparent activation energy without the definition of a detailed model for the reaction pathway. This seems to be the way of choice to bypass the model-inherent problems. But also in this case assumptions are necessary for a scientifically useful result. For instance, one assumption is that the same product is obtained irrespective of the heating rate. Accordingly, the isoconversional methods, which allow for model-independent estimates of the apparent activation energy at progressive degrees of conversion by conducting multiple experiments at different constant heating rates, are highly recommended in order to obtain a reliable kinetic description of the investigated process [14].

The differential isoconversional method suggested by Friedman [7] is based on Eq. (5) in the logarithmic form:

$$\ln\left[\beta_i\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha,i}\right]=\ln[A_\alpha f(\alpha)]-\frac{E_{a,\alpha}}{RT_\alpha}. \tag{7}$$

The apparent activation energy (E_a) is determined from the slope of the plot of $\ln[\beta_i(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,i}]$ versus $1/T_\alpha$, at a constant α value. Subscript i is the ordinal number of an experiment performed at a given heating rate. This method is rather accurate because it does not include any mathematical approximations.

3.2. Reaction model determination

3.2.1. Malek's kinetic procedure

The isoconversional method can be applied without knowledge of true $f(\alpha)$ function. But this function must be invariant for all heating rates. If this basic assumption is not fulfilled, an apparent E_a value would be calculated, which differs from the actual value. The invariance can be examined by the method which is offered by Málek [8–10]. He has suggested that $f(\alpha)$ function is proportional to the $y(\alpha)$ and $z(\alpha)$ functions that can simply be obtained by a simple transformation of thermogravimetric (TG) data. In non-isothermal conditions, these functions are defined as

$$y(\alpha)=\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\times\exp\left(\frac{E_a}{RT}\right), \tag{8}$$

$$z(\alpha)=p\left(\frac{E_a}{RT}\right)\times\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\times\frac{T}{\beta}, \tag{9}$$

where $p(E_a/RT)$ is the expression of the temperature integral. It was suggested that $p(E_a/RT)$ may be accurately estimated by means of the fourth rational expression of Senum and Yang [16]:

$$p(x)=\frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120}, \tag{10}$$

where x is reduced apparent activation energy (E_a/RT). For practical reasons, the $y(\alpha)$ and $z(\alpha)$ functions are normalized within the $(0,1)$ ranges. However, as evident from Eqs. (8) and (9) for calculations of $y(\alpha)$ and $z(\alpha)$ functions it is necessary to know the apparent activation energy in the case of non-isothermal conditions. Thus, by plotting the $y(\alpha)$ dependence, normalized within the $(0,1)$ range, the shape of the function $f(\alpha)$ is obtained. The $y(\alpha)$ function is therefore characteristic for a given reaction model, and it can be used as a diagnostic tool for reaction model determination. The mathematical properties of the $y(\alpha)$ function for basic kinetic models are summarized in Table 1. The $z(\alpha)$ function has a maximum at α_p^∞ for all reaction models summarized in Table 1. This parameter has characteristic values for basic reaction models and these values are summarized in Table 1.

If there are considerable differences in the shape of the $y(\alpha)$ and $z(\alpha)$ functions then, we can conclude that the assumption in which the reaction model was considered to be a single-step model has not fulfilled.

The calculated model-independent value of the apparent activation energy delivers an unambiguous choice of the appropriate kinetic model. A non-linear regression analysis with a fixed apparent activation energy value or an analysis using $y(\alpha)$ and $z(\alpha)$ functions [8] are suitable.

3.3. Determination of the pre-exponential (frequency) factor

Based on the determined apparent activation energy (E_a) and reaction (conversion) model ($g(\alpha)$), the A value can be calculated from Eq. (6), in accordance with dependence $g(\alpha)$ versus $E_a p(x)/R\beta$. For calculation the A value for the investigated decomposition process, the fourth rational expression of Senum and Yang [16] for $p(x)$ function was used. Also, knowing the value of the apparent activation energy and the kinetic model, the pre-exponential factor can be calculated from Eq. (11) [8]:

$$A = -\frac{\beta x_p}{T f'(\alpha_p)} \exp(x_p), \tag{11}$$

where $x_p = E_a/RT_p$ (T_p is the peak temperature on corresponding differential thermogravimetric, DTG curve), $f'(\alpha)$ is the differential form of the kinetic model [$\mathrm{d}f(\alpha)/\mathrm{d}\alpha$], α_p is the degree of conversion corresponding to the maximum on DTG curve and p represents the maximum of DTG curve.

4. Determination of distributed reactivity model

For estimation the DRM for investigated non-isothermal decomposition process of potassium metabisulfite, the Miura's procedure [11,12] is used.

In accordance with this procedure, the cumulative weight loss can be expressed by the following equation:

$$\frac{m_0 - m_t}{m_0} = 1 - \alpha = \int_0^\infty \exp\left[-A\int_0^t \exp\left(-\frac{E_a}{RT}\right)\mathrm{d}t\right] f(E_a)\,\mathrm{d}E_a, \tag{12}$$

where $f(E_a)$ is a distribution curve of the apparent activation energy and A is the pre-exponential (frequency) factor corresponding to the E_a value. The distribution curve $f(E_a)$ is normalized to satisfy

$$\int_0^\infty f(E_a)\,\mathrm{d}E_a = 1. \tag{13}$$

Specific mathematical forms of $f(E_a)$ appearing in the literature are the Gaussian [17–19], Weibull [20] and Gamma distributions [21–25]. The distribution can also be a finite discrete distribution of arbitrary form, in which case the integral in Eq. (12) would be replaced with a summation [26,27]. Knowing $f(E_a)$ and A, we can calculate the change in α for any heating profile. In general case, the pre-exponential factor (A) is assumed to be a constant to avoid the complexity of the analysis. However, the assumption of a constant A value may not be valid when $f(E_a)$ spreads over a wide range of E_a values, since that A and $f(E_a)$ are interrelated [18].

The procedure for estimation both $f(E_a)$ and A can be summarized in the following few items [11,12]:

(a) Measure α versus T relationships at least three different heating rates.
(b) Calculate the values of $\mathrm{d}\alpha/\mathrm{d}T$ at several but same α values at the different heating rates, then make Friedman plots ($\ln[\beta(\mathrm{d}\alpha/\mathrm{d}T)]$ versus $1/T$) at the same α values using the relationship in Eq. (7).
(c) Determine the apparent activation energies from the Friedman plots at different levels of α, then plot α against the apparent activation energy (E_a).
(d) Differentiate the α versus E_a relationship by E_a to give $f(E_a)$, since the following relation holds approximately:

$$\alpha = 1 - \int_{E_a}^\infty f(E_a)\,\mathrm{d}E_a = \int_0^{E_a} f(E_a)\,\mathrm{d}E_a. \tag{14}$$

(e) Calculate A corresponding to each E_a value at all heating rates β_i ($i = 1, 2, 3, \ldots$) using the following equation [12]:

$$\frac{0.545\beta_i E_a}{ART^2} = \exp\left(-\frac{E_a}{RT}\right) \tag{15}$$

and then employ the average A value as a true A value.

Eq. (15) was obtained when approximating Eq. (12) by Eq. (14). No *a priori* assumptions were required for the functional forms of $f(E_a)$ and $A(E_a)$. In other words, we could estimate A and E_a at any levels of α by using the above procedure.

5. Results and discussion

The TG and DTG curves of the decomposition process of potassium metabisulfite samples obtained at different heating rates (2.5, 5, 10, 15 and 30 °C min^{-1}) are shown in Fig. 1(a) and (b).

The effect of heating rate on the TG behavior of $K_2S_2O_5$ samples in nitrogen atmosphere is presented in Fig. 1. Lowering of the heating rate brings the reaction system closer to equilibrium conditions and minimizes the effects of heat transfer and thermal lag. As a result, the reaction starts and ends at lower temperatures, and decomposition occurs over a narrower temperature range.

The observed TG curves show an asymmetric character (Fig. 1(a)) and were moves to higher temperatures with increase in heating rate. Fig. 2 shows the relationships of α versus T at five different heating rates ($\beta = 2.5$, 5, 10, 15 and 30 °C min^{-1}).

Fig. 2 shows the temperature range in which the decomposition process occurs at considered values of heating rates ($145\,^\circ\mathrm{C} \leqslant T \leqslant 275\,^\circ\mathrm{C}$). From Fig. 2, it can be observed that all $\alpha - T$ curves at all considered heating rates has the same shapes.

Values of peak temperature (T_p) and the degree of conversion at maximum reaction rate (α_p), at various heating rates are presented in Table 2.

Increasing of heating rate leads to increase of the peak temperature value (T_p) from 210 to 250 °C. On the other

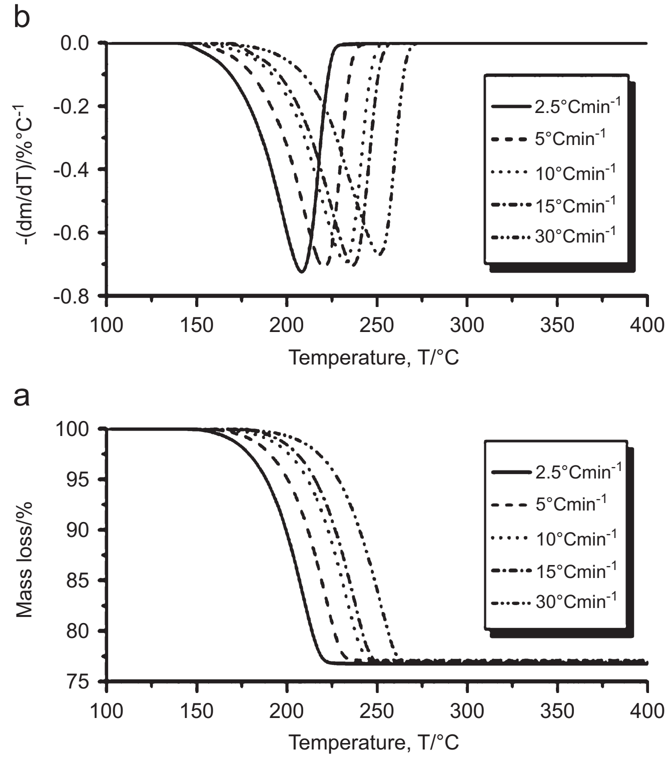

Fig. 1. TG (a) and DTG (b) curves for the thermal decomposition process of potassium metabisulfite samples in nitrogen atmosphere.

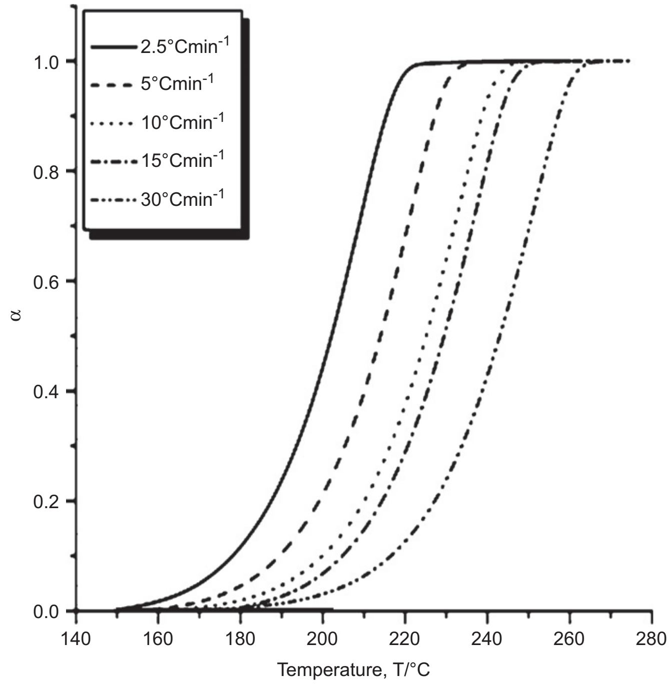

Fig. 2. The experimental conversion ($\alpha - T$) curves for the thermal decomposition process of potassium metabisulfite samples in nitrogen atmosphere, at the different heating rates.

hand, the values of α_p vary in the range of $0.73 \leqslant \alpha_p \leqslant 0.74$. The values of α_p at 2.5 and 5 °C min^{-1} are equal ($\alpha_p = 0.73$), while the value of α_p at 10, 15 and 30 °C min^{-1} is a little higher ($\alpha_p = 0.74$). It can be pointed out, that Lee and Dollimore [28] are established the procedure for choosing a reaction model from the degree of conversion at the maximum reaction rate (α_p). This approach has not gained wide use. Therefore, Vyazovkin and Wight [15] have recommended using isoconversional methods instead of modelistic approaches.

Table 2
Values of T_p and α_p for decomposition process of potassium metabisulfite determined by thermogravimetric analysis at different heating rates

Heating rate, β (°C min^{-1})	T_p (°C)	α_p
2.5	210	0.73
5	220	0.73
10	235	0.74
15	240	0.74
30	250	0.74

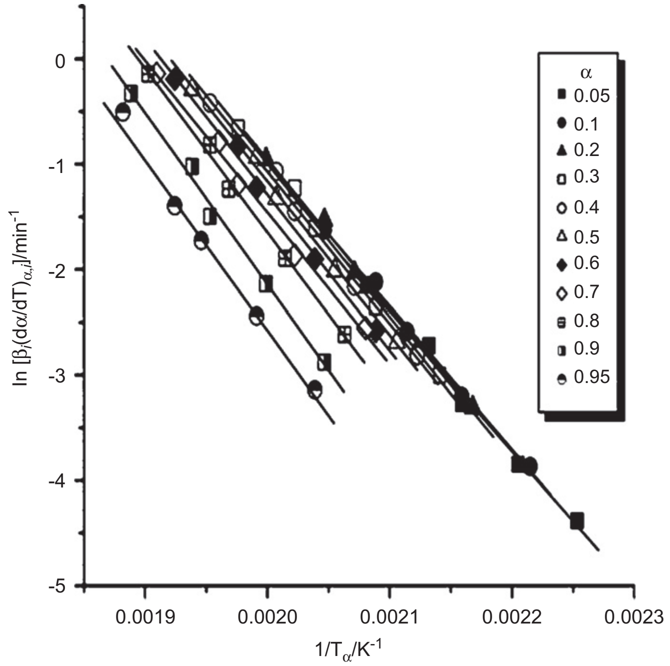

Fig. 3. Typical Friedman's isoconversional plots for the determination of an apparent activation energy at different conversion levels, for the non-isothermal decomposition process of potassium metabisulfite.

The non-isothermal decomposition process of potassium metabisulfite was analyzed by differential (Friedman) isoconversional method.

A typical Friedman plots, constructed to evaluate the slopes $\mathrm{d}(\ln\beta(\mathrm{d}\alpha/\mathrm{d}T))/\mathrm{d}(1/T)$, are presented in Fig. 3.

If the conversion mechanisms are the same at all conversion lavels, the isoconversion lines would all have the same slopes. From Fig. 3, we can observe that the isoconversional lines at all considered conversion lavels (see the inset in Fig. 3) have almost the same slopes.

The dependence of apparent activation energy (E_a) on the degree of conversion (α) (E_a–α plot) for non-isothermal decomposition process of potassium metabisulfite obtained

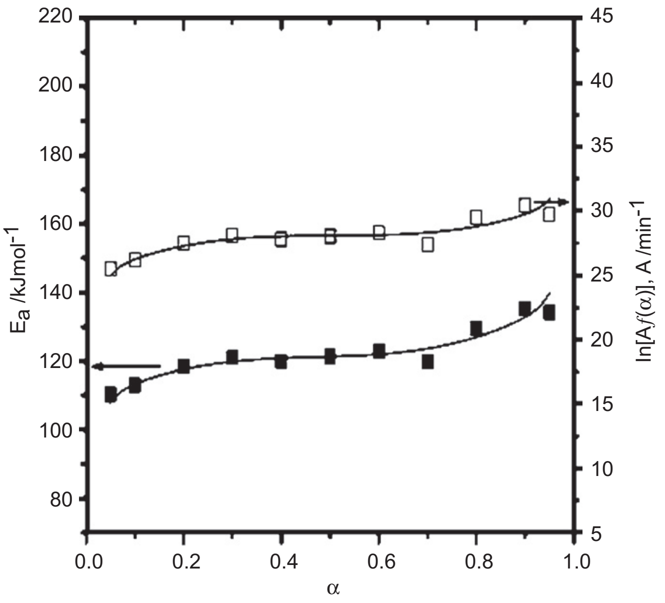

Fig. 4. Determined apparent activation energy (■) and apparent isoconversional intercepts (□) as a function of degree of conversion. The solid continuous lines represents the simulated trends of both, the apparent activation energy and isoconversional intercept with the degree of conversion.

by Friedman's method is presented in Fig. 4. The same figure (Fig. 4) also shows the dependence of the apparent isoconversional (Friedman) intercepts (Eq. (7)) on the degree of conversion (α) for the investigated decomposition process.

The symbols (■) and (□) represent directly calculated values of apparent activation energies and isoconversional intercepts from Friedman's equation, respectively. On the other hand, the full lines which are showed at the same figure, represents the simulated trends of both, the apparent activation energy and isoconversional intercept with the degree of conversion. The simulated lines have been drawn to better expose the changes of E_a values with progress of α during the transformation.

It was observed from Fig. 4 that the apparent activation energy was not really changed and almost independent with respect to the level of a conversion. This suggests that the non-isothermal decomposition process of potassium metabisulfite follow a single-step reaction. The apparent activation energy was determined as $E_a = 122.4 \pm 2.1\,\text{kJ mol}^{-1}$. It should be noticed that this result was obtained without any knowledge of the reaction model, $f(\alpha)$.

Furthermore, the variation of $y(\alpha)$ and $z(\alpha)$ functions with conversion are indicated in Figs. 5 and 6, calculated using Eqs. (8) and (9), respectively. We normalized the values of both $y(\alpha)$ and $z(\alpha)$ within (0, 1) interval under non-isothermal conditions for the decomposition process of potassium metabisulfite.

The shapes of the $y(\alpha)$ and $z(\alpha)$ plots are the practically unchanged with respect to heating rate. For calculations of the above functions, the apparent activation energy value of $E_a = 122.4\,\text{kJ mol}^{-1}$ evaluated from Friedman's method was used.

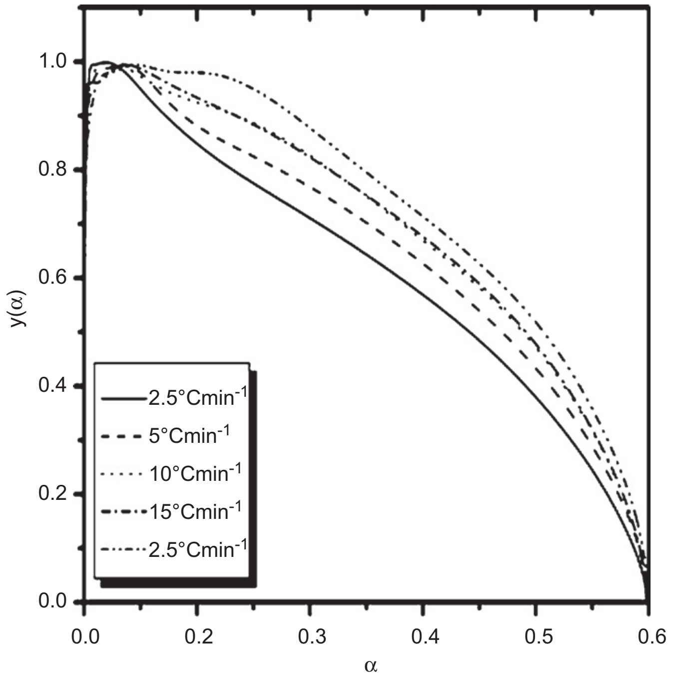

Fig. 5. Normalized $y(\alpha)$ function obtained by transformation of TG data for the decomposition process of potassium metabisulfite at the different heating rates ($\beta = 2.5$, 5, 10, 15 and 30 °C min^{-1}).

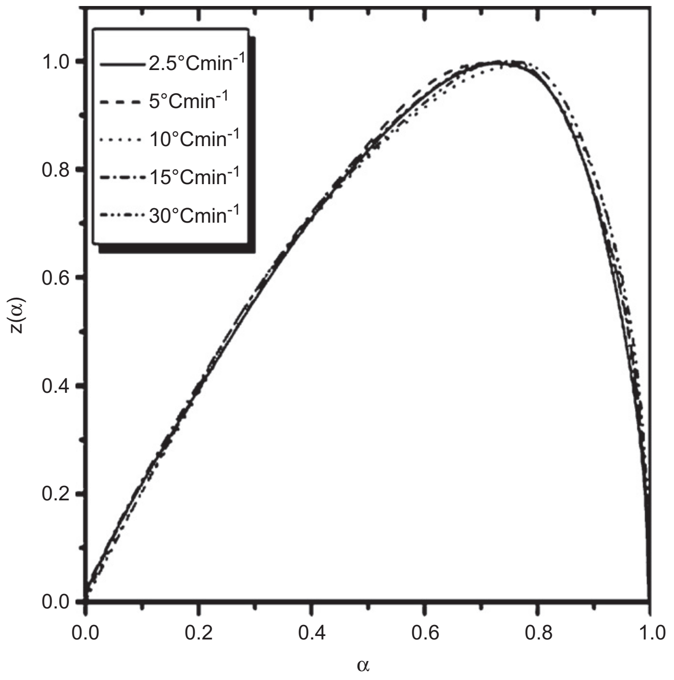

Fig. 6. Normalized $z(\alpha)$ obtained by transformation of TG data for the decomposition process of potassium metabisulfite at the different heating rates ($\beta = 2.5$, 5, 10, 15 and 30 °C min^{-1}).

The conversions, in which the $y(\alpha)$ and $z(\alpha)$ functions exhibit the maximum values (α_m and α_p^∞, respectively) for the different heating rates, are listed in Table 3.

Table 3
The conversions, in which the $y(\alpha)$ and $z(\alpha)$ functions exhibit the maximum values (α_m and α_p^∞, respectively) for different heating rates

Heating rate, β (°C min^{-1})	α_m	α_p^∞
2.5	0.05	0.74
5	0.07	0.73
10	0.03	0.75
15	0.07	0.74
30	0.08	0.75

As was noticed, the data in Table 3 which has been extracted from Figs. 5 and 6, show that α_m and α_p^∞ values weakly depend on the heating rate. The maxima of $y(\alpha)$ and $z(\alpha)$ plots fall into the small range of $0.03 \leqslant \alpha_m \leqslant 0.08$ and $0.73 \leqslant \alpha_p^\infty \leqslant 0.75$, respectively. The $y(\alpha)$ functions shows the convex behavior, whereas the maxima of $z(\alpha)$ functions has a values from 0.73 to 0.75, which corresponds to the R2 kinetic model (Table 1). The most probable kinetic model for decomposition process of potassium metabisulfite is therefore R2 model (with accommodation parameter $n = 2$).

By introducing the derived reaction model, $g(\alpha) = 1-(1-\alpha)^{1/2}$, into Eq. (6), Eq. (16) is obtained:

$$1 - (1 - \alpha)^{1/2} = \frac{AE_a}{R\beta} p(x). \tag{16}$$

The plot of $[1-(1-\alpha)^{1/2}]$ against $(E_a/R\beta)p(x)$ at the different heating rates is constructed in Fig. 7. By using Eq. (16), the A value was determined from the slope of the fitted line shown in Fig. 7.

For contracting area model (R2 with $n = 2$) and $E_a = 122.4\,\text{kJ mol}^{-1}$, the pre-exponential (frequency) factor was found to be $A = 1.37 \times 10^{12}\,\text{min}^{-1}$ ($\ln A = 27.95$). The obtained value of $\ln A$ is in good agreement with average value of Friedman isoconversional intercept ($\ln[Af(\alpha)] = 28.04$; Fig. 4).

The values of $f'(\alpha_p)$ (for R2 kinetic model) and pre-exponential factors (A) calculated from Eq. (11) at all considered heating rates are listed in Table 4.

From Table 4, it can be observed that very good agreement exists between the calculated values of A (including and average value) from the above mentioned equation and the value of A estimated from Eq. (16).

Therefore, the corresponding kinetic equation for describing the non-isothermal decomposition process of potassium metabisulfite is given by

$$\beta \frac{d\alpha}{dT} = 1.37 \times 10^{12} \times \exp\left(-\frac{122.4}{RT}\right)[2(1-\alpha)^{1/2}], \tag{17}$$

where $2(1-\alpha)^{1/2}$ represent the differential form of phase-boundary controlled reaction model.

As we mentioned in introduction section, the degree of conversion (α) is related to $f(E_a)$ by Eq. (14). Therefore, $f(E_a)$ is given by differentiating Eq. (14) by E_a as

$$f(E_a) = \frac{d\alpha}{dE_a}. \tag{18}$$

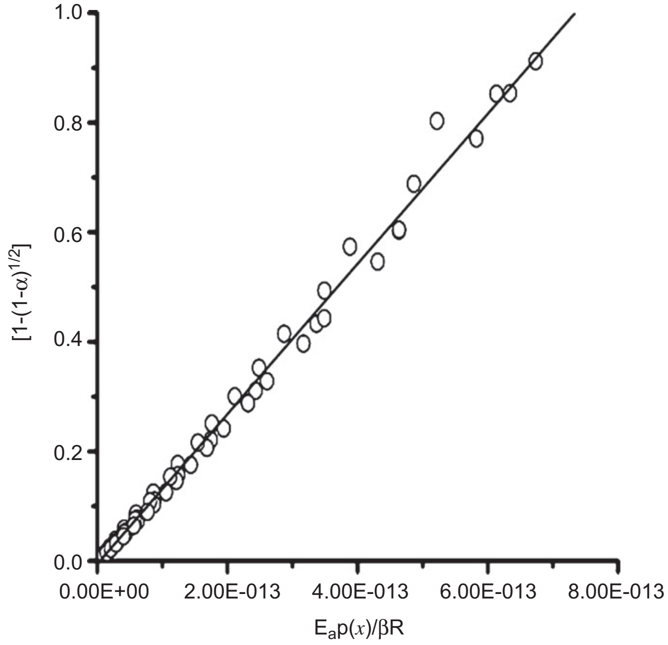

Fig. 7. Determination of A value by plotting $[1-(1-\alpha)^{1/2}]$ against $E_a p(x)/\beta R$ at $n = 2$ for the decomposition process of potassium metabisulfite at the different heating rates (β).

Table 4
Values of $f'(\alpha_p)$ (R2 or F1/2 kinetic model) and A calculated from Eq. (11) at different heating rates (β) for decomposition process of potassium metabisulfite

β (°C min^{-1})	$f'(\alpha_p)$	A (min^{-1})
2.5	−1.9625	1.37×10^{12}
5	−2.2127	1.26×10^{12}
10	−2.2705	9.59×10^{11}
15	−2.2867	1.06×10^{12}
30	−2.2554	1.19×10^{12}
Average	−2.1976	1.17×10^{12}

This equation shows that $f(E_a)$ can be obtained by differentiating the α versus E_a relationship, which may be deduced from Fig. 4. The graphically estimated distribution curve, $f(E_a)$, for the investigated decomposition process is presented in Fig. 8.

From Fig. 8, it can be observed that the estimated curve (Eq. (18)) for investigated process represents the very sharply and symmetrical distribution curve. The obtained distribution curve does not show the broad peak and the apparent activation energy does not spreads in the large E_a interval. The peak position is placed in unique point at $E_{a,p} = 121.3\,\text{kJ mol}^{-1}$. These results indicates that $f(E_a)$ can be represented by a single Gaussian distribution. By applying the non-linear least-squares analysis the Gaussian reactivity model is founded for considered system, and can be presented in form of Eq. (19):

$$f(E_a) = (2\pi)^{-1/2}\sigma^{-1} \exp\left[-\frac{(E_a - E_0)^2}{2\sigma^2}\right], \tag{19}$$

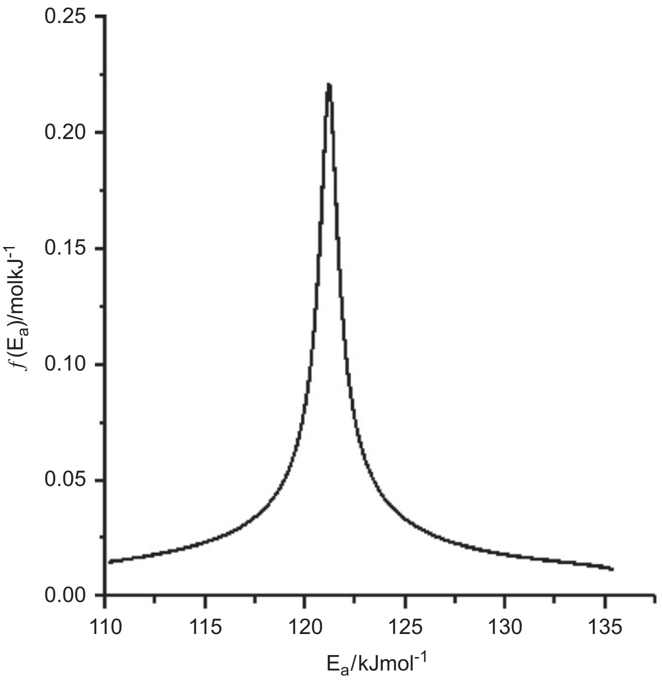

Fig. 8. The estimated distribution curve, $f(E_a)$, from the dependence α versus E_a for the decomposition process of potassium metabisulfite.

where E_0 and σ represents the mean apparent activation energy and standard deviation, respectively. Using the conventional non-linear least-squares analysis, the following values of Gaussian distribution parameters are obtained: $E_0 = 121.3\,\mathrm{kJ\,mol^{-1}}$ and $\sigma = 1.5\,\mathrm{kJ\,mol^{-1}}$. It can be pointed out, that obtained value of E_0 is a very similar to the value of E_a calculated by the differential (Friedman) isoconversional method ($122.4\,\mathrm{kJ\,mol^{-1}}$). Fig. 9 shows the comparison between the estimated distribution curve and calculated distribution curve assuming the Gaussian model (Eq. (19)).

It can be seen from Fig. 9 that exist very good agreement between estimated distribution curve (Eq. (18)) and calculated distribution curve with Gaussian function (Eq. (19)). After this analysis, the A values were estimated using Eq. (15) at the five heating rates, and the average values of A are plotted against E_a in Fig. 10.

From Fig. 10, we can see that the compensation effect [29,30] holds between the A values and E_a. The appearance of compensation effect shows that only one reaction model is presented [31]. The A value varies from an order of 10^{10} to an order of $10^{13}\,\mathrm{min^{-1}}$, and this result shows that A cannot be assumed as a constant for the investigated non-isothermal decomposition process. However, we can see from Fig. 10 that the greatest number of A values were grouped about the order of 10^{12}, which corresponds to the narrow range of E_a ($E_a = 119.9$–$123.0\,\mathrm{kJ\,mol^{-1}}$). This result is in agreement with order of A calculated using Eqs. (11) and (16).

To examine the validity of the presented Gaussian reactivity model, the experimental $\alpha{-}T$ curves at $\beta = 10$ and $30\,^{\circ}\mathrm{C\,min^{-1}}$ were compared with the calculated curves for the non-isothermal decomposition process of potassium metabisulfite, as shown in Fig. 11. The calculated curves was obtained by numerically integrating Eq. (12) using the evaluated $f(E_a)$ (Eq. (19)) and A versus E_a relationship estimated by the above procedure. It can be pointed out,

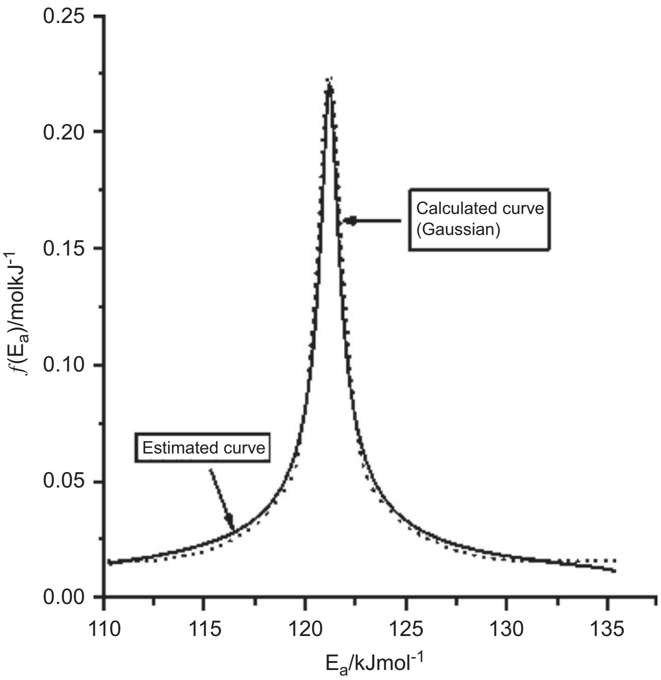

Fig. 9. Comparison of the estimated (Eq. (18)) and calculated (Eq. (19)) $f(E_a)$ curves for the non-isothermal decomposition process of potassium metabisulfite.

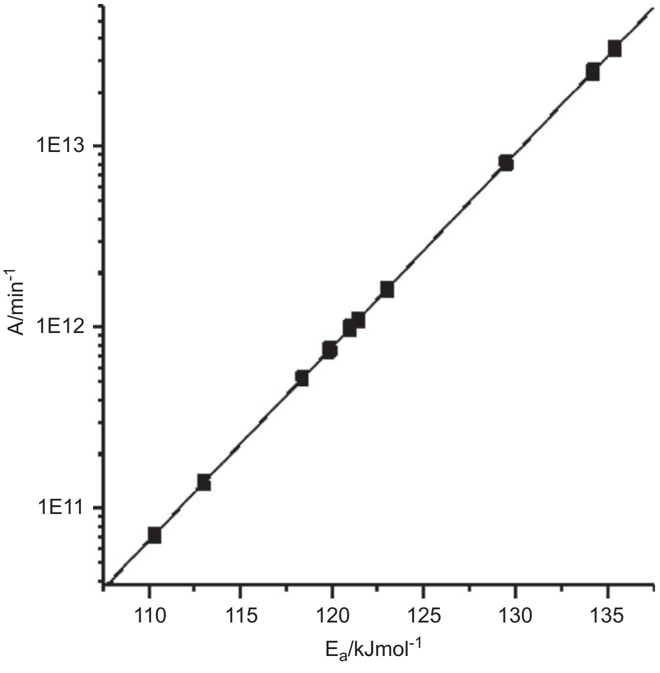

Fig. 10. Estimated average values of pre-exponential (frequency) factors from five different heating rates (Eq. (15)) as a function of apparent activation energy, for the decomposition process of potassium metabisulfite.

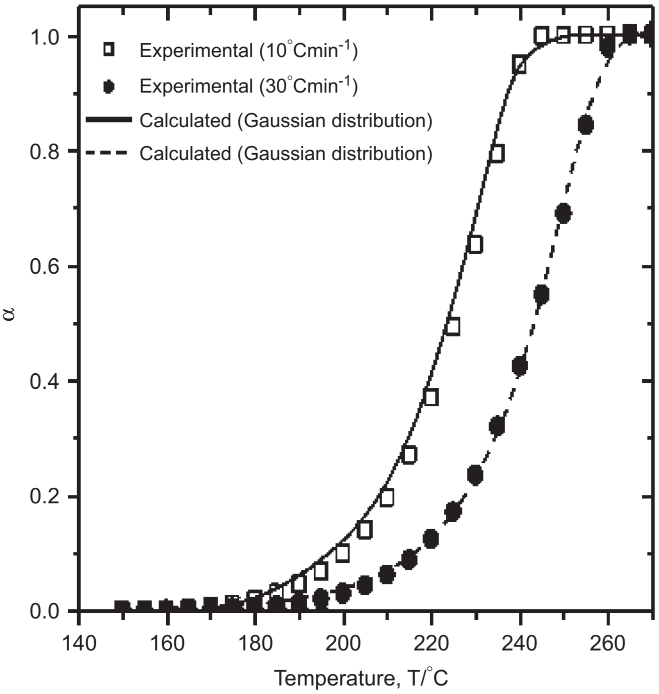

Fig. 11. Comparison between the experimental conversion ($\alpha - T$) curves and conversion curves reproduced using calculated $f(E_a)$ in the form of Gaussian distribution (with parameters: $E_0 = 121.3\,\mathrm{kJ\,mol^{-1}}$ and $\sigma = 1.5\,\mathrm{kJ\,mol^{-1}}$) for the approximated R2 (F1/2) reaction model, at $\beta = 10$ and $30\,^{\circ}\mathrm{C\,min^{-1}}$.

that calculated $\alpha - T$ curves are evaluated from the fact that the specific nature of $A - E_a$ compensation law causes the integration of the Gaussian distribution of the first-order reaction to look like as one-half order reaction (R2 or F1/2). Namely, this approximation is necessary because the value of pre-exponential factor (A) does not strictly constant (which is the basic condition for integration of the Gaussian distribution). In addition, this deviation is more expressive at the lower and at the higher values of degree of conversion (α) (Figs. 4 and 10).

Fig. 11 clearly shows that exist good agreement between the experimental and calculated $\alpha - T$ curves, which indicates that Gaussian reactivity model can be applied for analyzing of non-isothermal decomposition process of potassium metabisulfite.

It can be pointed out that Eqs. (14) and (15) implicitly assume that the E_a values differ for different α values. The $f(E_a)$ distribution curve used in the model calculation (Eq. (19) and Fig. 9) satisfy this assumption, but almost the same E_a value can be obtained for a considered range of α when we applied the above calculation method. In that case, a single-step reaction covers the considered α range and the A value can be estimated directly from the Friedman's equation (Eq. (7)) if the reaction model is known (determined the analytical form of $f(\alpha)$ function). The extreme case when the absolutely the same E_a value is obtained for all considered α values does not occurs in investigated decomposition process of potassium metabisulfite. Namely, if we look Fig. 4 carefully, we can observe that the obtained E_a values does not lay on strictly one straight line, but vary about that imagined straight line. It can be observed that mentioned deviations are higher at the beginning and at the end of investigated decomposition process ($\alpha = 0.05$–0.10 and $\alpha = 0.80$–0.95, respectively), but these deviations are in the limits of experimental error. On the other hand, a variation in apparent activation energy could be observed for both elementary and complex reactions. An elementary reaction could show variable apparent activation energy during its progress due to the heterogeneous nature of the solid sample, which could cause a systematic change in reaction kinetics due to product formation, crystal defect formation, intra-crystalline strain or the other similar effects.

It can be pointed out, that Friedman method tends to overestimate the mean apparent activation energy at midconversion ($E_{a,\mathrm{FR}} = 122.4\,\mathrm{kJ\,mol^{-1}} > E_0 = 121.3\,\mathrm{kJ\,mol^{-1}}$). Therefore, the increase in A above the true value at midconversion can be interpreted as a needed compensation effect required to recover the correct overall reactivity (Fig. 10). In addition, it was showed that the Friedman method can be applied to reactions which can be described by a narrow distribution of apparent activation energies ($\sigma \leqslant 4\%$ of E_0 value) [17]. From the results given above, we can conluded that the Friedman' method represents the appropriate kinetic method for the isoconversional (model-free) analysis of the investigated decomposition process. In fact, from the results obtained by applying the Friedman's method, we were established the narrow distribution curve of apparent activation energies, $f(E_a)$, which corresponds to the Gaussian distribution of reactivity with $\sigma < 4\%$ of E_0 value ($\sigma = 1.2\%$ of E_0; see the values of σ and E_0). Accordingly, these results confirm the statement, that the Friedman's method can be applied for the reactions which can be described with a narrow distribution of apparent activation energies. We can concluded that the E_a values calculated by the Friedman's method and estimated distribution curve, $f(E_a)$, are correct even in the case when the investigated decomposition process occurs through the single-step reaction mechanism.

For the non-isothermal decomposition process of potassium metabisulfite in nitrogen atmosphere, the following kinetic triplet was obtained: $E_a = 122.4\,\mathrm{kJ\,mol^{-1}}$, $A = 1.37 \times 10^{12}\,\mathrm{min^{-1}}$ and the phase-boundary model $f(\alpha) = 2(1-\alpha)^{1/2}$, which is associated with an inward advancement of the reaction interface from the crystal's edges (with $n = 2$ for reactions spreading in two dimensions). If the surface growth is much faster than the rate of penetration into the crystal, then a coherent interface is formed between the decomposed outer layers and reactant. If the propagating interface penetrates into undecomposed reactant at a constant rate, then the kinetics is governed by phase-boundary controlled reaction (for value of accommodation parameter $n = 2$, the considered reaction was spreads in two dimensions (over a surface)) [32]. The equation of phase-boundary reaction model often provides an excellent fit to the decay period of a decomposition and is particularly effective when surface nucleation and surface growth occur rapidly and internal nucleation either does not occur or occurs only very slowly.

The investigated decomposition process can be well described by the single Gaussian reactivity model with following parameters: $E_0 = 121.3\,\mathrm{kJ\,mol^{-1}}$ and $\sigma = 1.5\,\mathrm{kJ\,mol^{-1}}$. It was established that the value of mean apparent activation energy (E_0) is in good agreement with value of E_a evaluated from the Friedman's isoconversional method ($122.4\,\mathrm{kJ\,mol^{-1}}$), which corresponds to the middle part of conversion (for $\alpha \approx 0.50$).

6. Conclusions

The kinetics of the non-isothermal decomposition of potassium metabisulfite was accurately determined from a series of thermoanalytical experiments at different constant heating rates. The apparent activation energy (E_a) was calculated by differential (Friedman) isoconversional method without previous assumption regarding the conversion model fulfilled by the reaction. It was found that the apparent activation energy is practically constant in the considered α range (for $0.05 \leqslant \alpha \leqslant 0.95$), and this suggesting that the investigated decomposition was a single-step process with value of $E_a = 122.4\,\mathrm{kJ\,mol^{-1}}$ obtained by Friedman method. By applying the Malek's procedure, the appropriate reaction model characterizing the process studied was established. The $y(\alpha)$ and $z(\alpha)$ functions exhibit maxima at α_m and α_p^∞, respectively. The maxima fall into the small range of $0.03 \leqslant \alpha_m \leqslant 0.08$ and $0.73 \leqslant \alpha_p^\infty \leqslant 0.75$, respectively. From the results obtained by Malek's procedure, the contracting area geometrical model (R2) (where the radial direction predominates) represents the most probable kinetic model for describing the decomposition process of potassium metabisulfite.

By applying the Miura's procedure, the DRM for investigated decomposition process was established. From dependence α versus E_a, the experimental distribution curve of apparent activation energies, $f(E_a)$, was estimated. From the basic characteristics of estimated $f(E_a)$, it was concluded that the investigated non-isothermal decomposition process can be represented by a single Gaussian distribution. By applying the non-linear least-squares analysis the Gaussian reactivity model is founded for considered system with following distribution parameters: $E_0 = 121.3\,\mathrm{kJ\,mol^{-1}}$ (the mean apparent activation energy) and $\sigma = 1.5\,\mathrm{kJ\,mol^{-1}}$ (standard deviation). It was established, that the value of E_0 is a similar to the value of E_a calculated by the differential (Friedman) isoconversional method. By applying the Miura's procedure, the A values were estimated at five different heating rates and the average A values are plotted against E_a. The linear relationship between the A and E_a values was established (compensation effect). Also, it was established that the E_a values calculated by the Friedman's method and estimated distribution curve, $f(E_a)$, are correct even in the case when the investigated decomposition process occurs through the single-step reaction mechanism.

As the final conclusion, the following kinetic triplet: $E_a = 122.4\,\mathrm{kJ\,mol^{-1}}$, $A = 1.37 \times 10^{12}\,\mathrm{min^{-1}}$ ($\ln A = 27.95$), $f(\alpha) = 2(1-\alpha)^{1/2}$ and the Gaussian distribution reactivity model ($f(E_a) = (2\pi)^{-1/2}\sigma^{-1} \times \exp[-(E_a - E_0)^2/2\sigma^2]$) with parameters $E_0 = 121.3\,\mathrm{kJ\,mol^{-1}}$ and $\sigma = 1.5\,\mathrm{kJ\,mol^{-1}}$ were established for the non-isothermal decomposition process of potassium metabisulfite.

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