Computational aspects of kinetic analysis.
Part C. The ICTAC Kinetics Project — the
light at the end of the tunnel?

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Abstract

The paper discusses the kinetic results, which the participants in the ICTAC Kinetics Project have produced from the provided isothermal and nonisothermal data on a hypothetical simulated process, as well as on the thermal decomposition of ammonium perchlorate. The majority of the participants have applied various model-free techniques that employ multiple sets of isothermal or/and nonisothermal data obtained at different temperatures or/and at different heating rates. These 'multi-set' methods have been very successful in detecting multi-step kinetics in the data provided. Fitting data to multi-step kinetic models has allowed the 'true mechanism' to be guessed for the simulated data. For the real data, the mechanistic guesses happened to be uncertain. Various 'multi-set' methods have allowed fairly consistent values of the Arrhenius parameters to be derived from isothermal and nonisothermal data. © 2000 Elsevier Science B.V. All rights reserved.

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"After the suffering of his soul, he will see the light [of life] and be satisfied by his knowledge..."
Isaiah 53:11

1. Introduction

Before judging the results of the ICTAC Kinetics Analysis Project [1], we have to state the usual expectations of kinetics analysis and whether they are justified. Kinetic analysis of solid state decompositions is usually based on a single-step kinetic equation [2]

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

where t is the time, T is the temperature, α is the extent of conversion, and $f(\alpha)$ is the reaction model. The explicit temperature dependence of the rate constant is introduced by replacing $k(T)$ with the Arrhenius equation, which gives

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right)f(\alpha) \quad (2)$$

where A (the pre-exponential factor) and E (the activation energy) are the Arrhenius parameters and R is the gas constant. For nonisothermal conditions, $d\alpha/dt$ in Eq. (2) is replaced with $\beta(d\alpha/dT)$, where β is the heating rate.

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Kinetic analysis is traditionally expected to produce an adequate kinetic description of the process in terms of the reaction model and the Arrhenius parameters. These three components ($f(\alpha)$, E, and $\ln A$) are sometimes called the 'kinetic triplet'. An experimentally found reaction model is often expected to identify the reaction mechanism. Then, it is often expected that a solid state process should be describable by a single pair of Arrhenius parameters that can be meaningfully interpreted in the context of, say, the transition state theory. Besides, the kinetic triplets derived from isothermal and nonisothermal kinetics are expected to be equal. Regrettably, we have to admit that all these expectations are not generally justified. The root cause here is that the basic kinetic concepts rest upon the assumption of single-step reaction that disagrees with the multi-step nature of reactions in the solid state.

Thermally stimulated reactions in the solid state usually involve multiple steps that contribute to the overall reaction rate that is measured in thermal analysis experiments. If a process involves several steps with different activation energies, the relative contributions of these steps to the overall reaction rate will vary with both temperature and extent of conversion. This means that the effective activation energy determined from thermal analysis experiments will also be a function of these two variables. Expectations that a solid state process can be described by a single pair of Arrhenius parameters are thus not generally justified [3]. Because multi-step kinetics cannot usually be reduced to Eq. (1), its use to determine $f(\alpha)$ would result in a reaction model that does not have a clear mechanistic meaning. For this reason, one cannot justify establishing the reaction mechanism from $f(\alpha)$, alone [4]. Also, we cannot justifiably expect identical values of the effective (i.e. temperature dependent) Arrhenius parameters to result from isothermal and nonisothermal experiments, which are necessarily conducted in different temperature regions [5].

If the traditional expectations are not generally justified, the question arises what we could justifiably expect from kinetics analyses. In our opinion, one may justifiably expect kinetic analysis to be capable of

- revealing complexities in the reaction kinetics and prompting some mechanistic clues

- adequately describing the temperature dependence of the overall reaction rate
- producing reasonably consistent kinetic characteristics from isothermal and nonisothermal data.

How are these 'justifiable expectations' met by today's methods of kinetic analysis? Modern kinetic analysis may be represented by two alternative approaches. For both isothermal and nonisothermal kinetics, the currently dominating approach appears to be force-fitting of experimental data to different reaction models. Following these indiscriminate model fitting methods, Arrhenius parameters are determined by the form of $f(\alpha)$ chosen. Such methods tend to fail to meet even the justifiable expectations [4,6]. The application of these methods to isothermal data gives rise to believable values of Arrhenius parameters that, however, are likely to conceal the kinetic complexity [4,5,6]. In a nonisothermal experiment both T and α vary simultaneously. The application of the model-fitting approach to single heating-rate data generally fails to achieve a clean separation between the temperature dependence, $k(T)$, and the reaction model, $f(\alpha)$. As a result, almost any $f(\alpha)$ can satisfactorily fit the data at the cost of drastic variations in the Arrhenius parameters, which compensate for the difference between the assumed form of $f(\alpha)$ and the true but unknown reaction model. For this reason, the application of the model-fitting methods to single heating-rate data produces Arrhenius parameters that are highly uncertain and, therefore, cannot be meaningfully compared with the isothermal values [4,5]. Unfortunately, for years, the model-fitting analysis of single heating-rate data has been the most prevalent computational technique in nonisothermal kinetics. That is why the failures of this technique have been mistaken for the failures of nonisothermal kinetics as a whole. Therefore, the consequent antagonistic attitude towards nonisothermal kinetics should be primarily blamed on the overwhelming use of this flawed computational technique.

An alternative approach to kinetic analysis is to use model-free methods that allow for evaluating Arrhenius parameters without choosing the reaction model. The best known representatives of the model-free approach are the isoconversional methods [7–9]. These methods yield the effective activation energy as a function of the extent of conversion.

Knowledge of the dependence E_α on α assists in both detecting multi-step processes and drawing certain mechanistic conclusions [3,10]. Secondly, it is sufficient to predict the reaction kinetics over a wide temperature region [3,6,10]. Thirdly, the isoconversional methods yield similar (but not identical!) dependences of the activation energy on the extent of conversion for isothermal and nonisothermal experiments [4,5]. In other words, the model-free isoconversional methods are capable of meeting the above-mentioned justifiable expectations. It is, therefore, very satisfying to note that the majority of the participants in the project have used various isoconversional techniques for kinetic computations.

For the ICTAC Kinetics Analysis Project, the present author has provided simulated data on a hypothetical process and experimental data on the thermal decomposition of ammonium perchlorate. The following sections discuss the results of the applications of both model-fitting and model-free methods to these data. A detailed description of the methods and data is given in Part A [11].

2. Isoconversional methods for isothermal and nonisothermal data

The isoconversional method of Friedman [7] presents the most straightforward way to evaluate the effective activation energy, E_α, as a function of the extent of reaction. This is a differential method, which can be applied to integral data (e.g. TG data) only after their numerical differentiation. Because this procedure may lead to erroneous estimates of the activation energy, the use of the integral isoconversional methods appears to be a safer alternative. For isothermal data, the E_α-dependence can be obtained from Eq. (3)

$$-\ln t_{\alpha,i} = \ln\left[\frac{A_\alpha}{g(\alpha)}\right] - \frac{E_\alpha}{RT_i} \tag{3}$$

which we call the 'standard' isoconversional method. Henceforth, the subscript α denotes values related to a given extent of conversion.

For nonisothermal conditions, integral isoconversional methods were proposed by Ozawa [8] and Flynn and Wall [9]. These methods are based on an oversimplified approximation of the temperature integral and need a correction for smaller values of E/RT [12]. To avoid inaccuracies associated with approximations of the temperature integral, Vyazovkin proposed a non-linear isoconversional method [13,14]. According to this method, for a set of n experiments carried out at different heating rates, the activation energy can be determined at any particular value of α by finding the value of E_α for which the function

$$\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i} \tag{4}$$

is a minimum. In Eq. (4), the temperature integral

$$I(E, T_\alpha) = \int_0^{T_\alpha} \exp\left(\frac{-E}{RT}\right)\mathrm{d}T \tag{5}$$

is determined by direct numerical integration.

3. Simulated data

Simulated data are the only data for which Arrhenius parameters and reaction models are known exactly. Therefore, the use of simulated data is, in fact, the only way to test a computational method. The data were simulated according to the scheme of two parallel first-order reactions

$$\begin{aligned} A &\rightarrow \text{products} \\ B &\rightarrow \text{products} \end{aligned} \tag{6}$$

It was also assumed that the both processes make equal contributions to α. The overall reaction rate of this process is

$$\begin{aligned} \frac{\mathrm{d}\alpha}{\mathrm{d}t} &= \frac{1}{2}\left(\frac{\mathrm{d}\alpha_1}{\mathrm{d}t} + \frac{\mathrm{d}\alpha_2}{\mathrm{d}t}\right) \\ &= \frac{1}{2}[k_1(T)(1-\alpha_1) + k_2(T)(1-\alpha_2)] \end{aligned} \tag{7}$$

The Arrhenius parameters of the individual steps were taken so that A_1 is equal to $10^{10}\,\mathrm{min}^{-1}$, E_1 to $80\,\mathrm{kJ\,mol}^{-1}$; A_2 to $10^{15}\,\mathrm{min}^{-1}$ and E_2 is equal to $120\,\mathrm{kJ\,mol}^{-1}$. These values were chosen to make the rates of the two steps are comparable within the working range of temperatures. Integration of Eq. (7) for isothermal and nonisothermal conditions has given rise to respective dependences of α versus t and of α versus T.

The effective activation energy of the overall process (6) is

$$E_\alpha = -R \left[\frac{d \ln (d\alpha/dt)}{dT^{-1}} \right]_\alpha$$

$$= \frac{E_1 k_1(T)(1-\alpha_1) + E_2 k_2(T)(1-\alpha_2)}{k_1(T)(1-\alpha_1) + k_2(T)(1-\alpha_2)}$$

(8)

which is clearly a function of both temperature and extent of conversion. Substitution of the dependences of α versus t for various T and of α versus T for various β into Eq. (8) allows surface plots of the effective activation energy as a function of α and T and/or β to be obtained. These plots are presented in Figs. 1 and 2.

The application of Eqs. (3) and (4) to the isothermal and nonisothermal data results in the E_α-dependences shown in Figs. 1 and 2. For the isothermal data, the E_α-dependence represents the E–α projection of the $E(\alpha, T)$ surface averaged over the temperature. The E_α-dependence derived from the nonisothermal data is the E–α projection of the $E(\alpha, \beta)$ surface averaged over the heating rate. Because the surfaces related to the isothermal and nonisothermal data have somewhat different shapes, one should not expect the respective E_α-dependences to be identical [5].

Fig. 2. Surface plot of activation energy as a function of extent of conversion and heating rate for data simulated for nonisothermal conditions.

3.1. Evaluating activation energies

Fig. 3 provides the results of the model-free isoconversional computations reported by various workers. For some reason, the application of this technique to the isothermal data did not attract much interest.
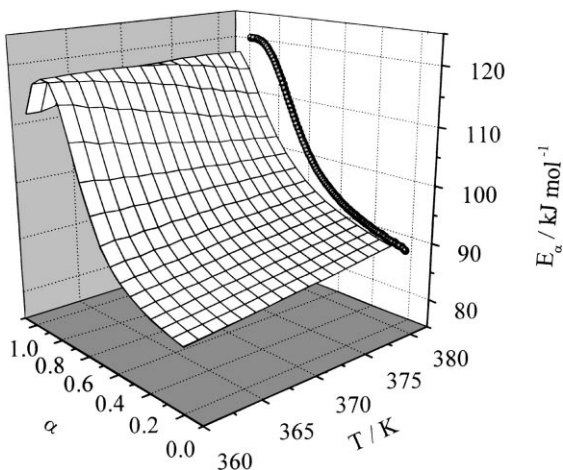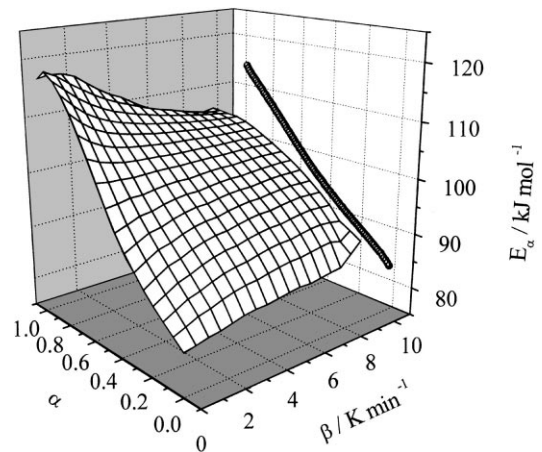

Fig. 1. Surface plot of activation energy as a function of extent of conversion and temperature for data simulated for isothermal conditions.
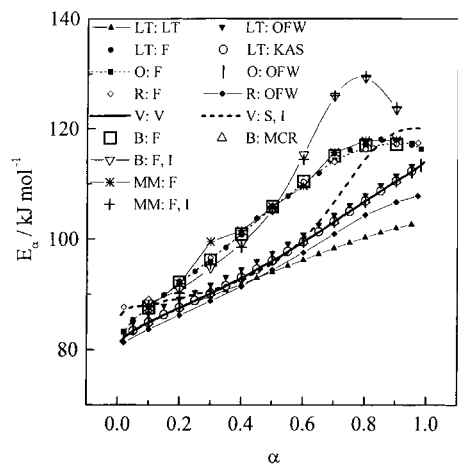

Fig. 3. Dependences of the activation energy on the extent of conversion determined by various isoconversional methods for simulated process. The letter codes stand for Worker: Method, Conditions (Workers, LT: Lee and Tang; O: Opfermann; R: Roduit; B: Burnham; MM: Málek and Mitsuhashi; V: Vyazovkin; Methods, F: Friedman; OFW: Ozawa, and Flynn and Wall; MCR: modified Coats and Redfern; KAS: Kissinger, Akahira and Sunrose; LT: Lee and Tang; S: standard isoconversional, Eq. (3), V: Vyazovkin; Conditions: I: isothermal; blank: nonisothermal).

Table 1
Kinetic triplets obtained by different workers for nonisothermal simulated data

Worker	E_1/kJ mol^{-1}	$\ln (A_1/s^{-1})$	$f_1(\alpha)$	E_2/kJ mol^{-1}	$\ln (A_2/s^{-1})$	$f_2(\alpha)$
A	100.4	25.09	F1.5[a]			
A	104.4	26.03	A0.75[b]			
B[c]	80.0	18.93	F1	120.0	30.44	F1
NS[c]	79.8	18.52	F1	120.4	30.55	F1
O	97.1	23.95	F1.291			
O[c]	79.54	18.79	F1	118.96	30.10	F1
R[c]	80.06	18.93	F1	120.04	30.42	F1
True values	80	18.93	F1	120	30.44	F1

[a] F followed by a number, n, stands for a reaction order model, $f(\alpha)=(1-\alpha)^n$.
[b] A followed by a number, n, stands for an Avrami–Erofeev model, $f(\alpha)=n(1-\alpha)[-\ln (1-\alpha)]^{(1-1/n)}$.
[c] Model of parallel reactions.

Nevertheless, it is very instructive to see that the application of various modifications of the isoconversional methods has resulted in consistent E_α-dependences. Almost all of the E_α-dependences showed variation in the activation energy between 80 and 120 kJ mol^{-1}. The observed dependences immediately suggest [10] the occurrence of a multi-step process that includes single steps with the estimated values of the activation energy ca. 80 and 120 kJ mol^{-1}. These extremes are practically equal to the true values of activation energy of the individual reactions involved in the multi-step kinetics.

As seen from Fig. 3, there are some rather insignificant differences between the E_α-dependences obtained by using integral and differential methods. These differences arise partially from the fact that the equations of the integral methods are usually derived under the assumption of the constancy of the activation energy. On the other hand, the differential methods may suffer from imprecise numerical differentiation, even in the case of artificial data that are free of 'experimental noise'. From Fig. 3 one can see that the application of Friedman's method to the isothermal simulated data yields E_α-values exceeding 120 kJ mol^{-1} that can only be explained as a computational artifact.

Burnham and Opfermann have refined the values of the activation energy by using secondary fitting data to multi-step kinetic models. This procedure uses the values of the activation energy obtained by a model-free isoconversional method as the initial estimates that are further optimized in the process of fitting data to assumed multi-step kinetic models. A minimum of the residual sum of squares is used as a criterion for optimization. The obtained values are in excellent agreement with the 'true' values (Tables 1 and 2).

Nomen and Sempere used an original model-free technique (so-called 'NPK method' [11]) that allowed them to detect the reaction complexity in the form of a temperature dependence of the activation energy. From Table 1 we can see that they obtained very good estimates for the 'true' values of the activation energy.

Table 2
Kinetic triplets obtained by different workers for isothermal simulated data

Worker	E_1/kJ mol^{-1}	$\ln (A_1/s^{-1})$	$f_1(\alpha)$	E_2/kJ mol^{-1}	$\ln (A_2/s^{-1})$	$f_2(\alpha)$
A	101.2	24.97	A0.75			
B[a]	80.1	18.94	F1	120.3	30.49	F1
O	99.3	24.71	F1.512			
O[a]	80.13	18.95	F1	120.28	30.50	F1
R[a]	79.94	18.93	F1	120.04	30.42	F1
True values	80	18.93	F1	120	30.44	F1

[a] Model of parallel reactions.

The correct values of the activation energies have also been found by Roduit (Tables 1 and 2), who unfortunately did not disclose the principle of the computations. All we know is that his methods is based on model-fitting of a series isothermal or/and nonisothermal data obtained at different temperatures or/and at different heating rates.

Anderson and Opfermann have attempted to describe the process by a single kinetic triplet obtained as a result of model-fitting (Tables 1 and 2). The kinetic complexity seems to have escaped the treatment applied by Anderson, who reported only constant values (100.4 and 104.4 kJ mol^{-1}) of the activation energy that can be thought of as the values averaged over α. The constant value of the activation energy found by Opfermann (97.1 kJ mol^{-1}) agrees well with the values found by Anderson. However, the statistical analysis performed by Opfermann suggests that multi-step kinetic models should be preferred over the averaged single-step treatment.

3.2. Guessing reaction mechanisms

The obtained E_α-dependences (Fig. 3) allow one to unmistakably recognize a multi-step process. Taken alone, this fact is already a very important piece of mechanistic information. Additionally, the shape of these dependences suggests [10] parallel reactions as a possible reaction mechanism. Burnham, Nomen and Sempere, Opfermann, and Roduit have tried to fit the simulated data to multi-step kinetic models. As we can see (Tables 1 and 2), they all have been quite successful in establishing the true 'reaction mechanism' of the simulated process. Málek and Mitsuhashi also have found the correct mechanism. Their conclusion is based on the analysis of the plots of $(d\alpha/dt)t$ versus α for isothermal data and $(d\alpha/dt)T^2$ versus α for nonisothermal data. A discussion of the mechanisms resulted from fitting of data to single-step models does not present much interest, because these mechanisms do not reflect the reaction complexity, which is the major mechanistic feature of the process considered.

3.3. Consistency of isothermal and nonisothermal data

It is seen from Fig. 3 that the E_α-dependences produced from isothermal and nonisothermal data

are in good agreement with each other. The same can be said about the results presented in Tables 1 and 2. Although fitting isothermal and nonisothermal data to single-step models resulted in incorrect values of the kinetic triplets (Tables 1 and 2), the latter are also in perfect agreement. Therefore, we should keep in mind that the consistency of the kinetic triplets derived from isothermal and nonisothermal data is not a sufficient condition for the kinetic triplets to be trustworthy.

4. Ammonium perchlorate data

The thermal decomposition of ammonium perchlorate (AP) is a good example of a real-life process that is as involved as it can possibly be. There is a plethora [15–18] of experimental information on this process, but very little agreement on its reaction kinetics and mechanisms. We have recently used isoconversional methods to study the kinetics of the thermal decomposition of AP under both isothermal and nonisothermal conditions [4,19].

4.1. Evaluating activation energies

The situation when the reaction mechanism is unknown is especially favorable for model-free methods that allow for kinetic evaluations without a priori guessing the reaction mechanism. Fig. 4 presents the E_α-dependences obtained by using various isoconversional methods. The process demonstrates a strong variation in the effective activation energy with the extent of reaction. As we can see, the unknown reaction mechanism has not been an obstacle for different workers to report consistent E_α-dependences. For nonisothermal decomposition, the activation energy decreases from ca. 115 to 120 kJ mol^{-1} at $\alpha \approx 0$ to ca. 85 (Vyazovkin), ca. 95 (Opfermann) and ca. 93 kJ mol^{-1} (Burnham) at $\alpha \approx 0.3$. Further decomposition is characterized by a monotonous increase in the activation energy to ca. 115 kJ mol^{-1} at $\alpha \approx 1$. This obviously suggests that the kinetics of nonisothermal decomposition are determined by at least two steps with noticeably different activation energies that can be roughly estimated as 85–95 and 115–120 kJ mol^{-1}, respectively. Isothermal decomposition shows (Fig. 4) somewhat different kinetics for the initial decomposi-
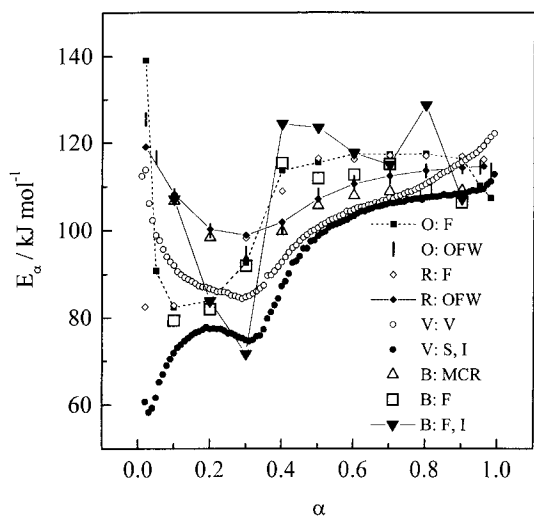
Fig. 4. Dependences of the activation energy on the extent of conversion determined by various isoconversional methods for the thermal decomposition of ammonium perchlorate. For abbreviations see Fig. 3.

tion stage ($\alpha < 0.3$) that is characterized by an increase in the activation energy from ca. 60–75 kJ mol^{-1}. We have recently given [4,19] an explanation for the differing kinetics under isothermal and nonisothermal conditions. Therefore, the kinetics of nonisothermal

decomposition are also determined by at least two steps with activation energies that can be estimated as approximately 60 and 110 kJ mol^{-1}.

Internal consistency of the activation energies evaluated by using the implicit multi-step kinetic models (Tables 3 and 4) may be estimated by their capability of reproducing the experimentally found E_α-dependence. This can be accomplished only if the limits of variation of the E_α-dependence do not exceed the region limited by the activation energies of the individual steps (i.e. E_1 and E_2). The activation energy evaluated by the isoconversional method for nonisothermal data spans ca. 93–109 (Burnham), ca. 95–115 (Opfermann), and ca. 85–115 (Vyazovkin) kJ mol^{-1}. As we can see from Table 3, not all of the reported models satisfy the above criterion of internal consistency. This problem is even more obvious in the case of the isothermal data, for which the experimentally evaluated E_α-dependence spans more than 50 kJ mol^{-1}; namely, 72–125 (Burnham) and 60–115 (Vyazovkin) kJ mol^{-1}. All the reported values of E_1 and E_2 (Table 4) lie inside the limits of the E_α variation, and, therefore, cannot be used to reproduce the experimentally found E_α-dependence. For instance, if the values of E_1 and E_2 reported by Opfermann can account for 40 kJ mol^{-1} of the

Table 3
Kinetic triplets obtained by different workers for nonisothermal decomposition of ammonium perchlorate

Worker	E_1/kJ mol^{-1}	ln (A_1/s^{-1})	$f_1(\alpha)$	E_2/kJ mol^{-1}	ln (A_2/s^{-1})	$f_2(\alpha)$
B[a]	97.59	17.11	$\alpha(1-\alpha)^{1.81}$	112.84	15.59	F0.294
Ns[a]	75.8	12.50	$\alpha^{0.98}(1-\alpha)^{3.53}$	121	15.42	$\alpha^{0.33}(1-\alpha)^{0.33}$
O[b]	93.0	14.39	A2.11	113.43	15.76	F0.363
O[a]	92.0	14.15	A2.26	112.60	15.58	F0.354
R[a]	99.49	15.623	A2.818	112.68	15.019	F0.467

[a] Model of parallel reactions.
[b] Model of consecutive reactions.

Table 4
Kinetic triplets obtained by different workers for isothermal decomposition of ammonium perchlorate

Worker	E_1/kJ mol^{-1}	ln (A_1/s^{-1})	$f_1(\alpha)$	E_2/kJ mol^{-1}	ln (A_2/s^{-1})	$f_2(\alpha)$
B[a]	82.53	13.21	$\alpha(1-\alpha)^{1.33}$	107.45	14.28	F0.0615
O[b]	66.46	8.57	A3.10	107.86	14.50	F0.202
O[a]	66.96	7.96	A3.57	105.76	14.00	F0.192
R[a]	99.28	15.170	A2.922	111.76	15.333	F0.205

[a] Model of parallel reactions.
[b] Model of consecutive reactions.

actual variation in E_α, the values found by Roduit account for a span of only 13 kJ mol^{-1}. The above suggests that the optimization procedures based exclusively on minimizing the deviation of a multi-step model from experimental measurements may be insufficient from the physical standpoint. These procedures should be backed up by an additional constraint, which is the condition of minimum deviation between the E_α-dependence that can be derived from the optimized multi-step model and the actual E_α-dependence that has been obtained by using a model-free method.

4.2. Guessing reaction mechanisms

As mentioned in the previous section, some of the two-step models cannot be used to reproduce the observed E_α-dependences (Fig. 4) and that may cast some doubts on the trustworthiness of the respective mechanisms. Furthermore, identification of the reaction models is noticeably more ambiguous as opposed to the case of the simulated data (compare Tables 3 and 4 with Tables 1 and 2). In the case of the real decomposition, we observe an obvious uncertainty in choosing the reaction models for individual steps (Avrami–Erofeev, reaction order, and autocatalytic models). Besides, we also face the problem of the uncertainty in the overall kinetic scheme of decomposition. For instance, Opfermann demonstrates that statistical analysis does not allow one to conclude unequivocally whether the process follows a model of two parallel or consecutive reactions. From the statistical point of view, both models fit the decomposition data equally well. Needless to say, the reaction mechanisms represented by these statistically indistinguishable models are absolutely different from the chemical standpoint.

The above example demonstrates that fitting data to reaction models cannot be used as the sole means of identifying the reaction mechanisms. Note that this is equally true in the case when statistical analysis allows one to unequivocally choose a single reaction model [4,6]. Statistical analysis evaluates the reaction models by the goodness of fit of the data, but not by the physical sense of applying these models to the experimental data. Even if a reaction model does not have any physical meaning at all, it may well be the best fit to the experimental data [4,6].

4.3. Consistency of isothermal and nonisothermal data.

Let us compare the reported values of the activation energy for the individual steps for isothermal and nonisothermal decompositions (Tables 3 and 4). The E_1 and E_2 values reported by Roduit are consistent for the isothermal and nonisothermal decompositions. The E_1 values found by Opfermann for isothermal and nonisothermal data are rather inconsistent. However, as we noted above, the E_1 and E_2 values reported by Opfermann show better internal consistency because they are potentially capable of better reproduction of the experimentally evaluated E_α-dependence. Again, we have to conclude that the consistency of the kinetic parameters derived from isothermal and nonisothermal data should not be used as a decisive criterion to determine if the values are trustworthy.

5. Conclusions

The most important feature of a reliable method of kinetic analysis is its ability to handle multi-step processes that are rather typical for reactions of solids. The model-free and model-fitting methods that use sets of isothermal or/and nonisothermal data obtained at different temperatures or/and at different heating rates are found to be very effective in detecting this feature in the data provided. The model-free methods reveal the kinetic complexity in the form of a dependence of the activation energy on the extent of conversion (isoconversional methods) or in the form of a temperature dependence (the NPK method). While too young to reveal all the ups and downs, the NPK method makes a promising debut. It is easy to appreciate the value of the isoconversional method, which is a seasoned veteran of kinetic battles. As seen from the results of the project, various isoconversional methods applied by different workers to the same set of nonisothermal data have produced consistent dependences of the activation energy on the extent of conversion. This fact bears a great meaning for nonisothermal kinetics that for years has been a subject of acidulous criticisms and humiliating mockery for its alleged inability to produce sensible kinetic data. The isoconversional methods may also be helpful in providing some mechanistic clues. However, one should

not forget that the mechanistic clues are not yet the reaction mechanism, but rather a path to it that can further be followed only by using species-specific experimental techniques.

The project has demonstrated the prevalent use of the methods that employ multiple sets of isothermal or/and nonisothermal data obtained at different temperatures or/and at different heating rates. Hopefully this reflects the actual tendency for the increasing use of these 'multi-set' methods in solid state kinetics. An extensive application of these methods to isothermal as well as to nonisothermal data would certainly enrich kinetics with a deeper insight into the multi-step nature of solid state reactions.

Acknowledgements

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