

INVERSE PROBLEMS OF SOLID STATE REACTION KINETICS: COMBINATION OF SIMPLE MODELS

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In homogeneous chemical kinetics, models of complicated reactions are constructed from models for simple reactions. This is not the case for solid-state reaction kinetics in which there is no conception of the simple reaction. Until very recently the routine was to use one-stage models (e.g. Avrami-Erofeev model) in analyzing experimental data. This practice was changed by the ICTAC Kinetic Project "Computational aspects of kinetic analysis"[1]. This fairly large-scaled project was organized similarly to 1983-year project [2] in homogeneous chemical kinetics, which proved the ambiguity in the interplay between the mechanism and the observed kinetic behaviour and contributed considerably into the new strategy of exploring mechanisms of homogeneous reactions. In the ICTAC Kinetic Project numerous multi-stage models have been tried, and one of important conclusions is that multi-stage models are more adequate. This conclusion is far from being unexpected, but suggested combinations of models are fairly arbitrary and raise a number of questions when considered from the angle of inverse kinetic problems.

When a two-stage model provides a better fit in comparison with each of one-stage models, an essential question is whether this is due to a conceptual improvement of the model or the result of the greater approximation flexibility alone. Table 1 illustrates one of numerous examples from the ICTAC Kinetic Project.

Table 1. Efficient activation energies (E_a ; kJ/mole) for the thermal decomposition of ammonium perchlorate found with the use of different models [1]

Combinations of models	Concurrent stages	Consecutive stages
Avrami equation	$n=3.57\pm 0.34$; $E_a=66.96\pm 0.76$	$n=3.10\pm 0.22$; $E_a=66.46\pm 0.83$
n-th order equation	$n=0.192\pm 0.02$; $E_a=105.76\pm 0.24$	$n=0.202\pm 0.02$; $E_a=107.86\pm 0.21$
1-st order equation with autocatalysis	$E_a=67.57\pm 0.31$	$E_a=74.08\pm 0.82$
n-th order equation	$n=0.191\pm 0.02$; $E_a=105.76\pm 0.24$	$n=0.204\pm 0.02$; $E_a=107.71\pm 0.20$

It is worth emphasizing, first of all, that the same rate equations are combined both as concurrent and as consecutive stages. The corresponding values of activation energies differ insignificantly, and accordingly there is no answer to the question which combination is more correct or more preferable. This fact as itself indicates essential problems in the combination of conventional rate equations. Also, within this approach the quantity of the activation energy, which has no clear physical meaning in solid state reaction kinetics and is permanently discussed [3], falls into two arbitrary items. And these items are practically the same irrespectively of whether concurrent or consecutive stages are concerned. The basis of this is not clear.

In Table 1, the first model is the Avrami equation. To discuss combinations of models, we need it in the differential form

$$\frac{d\alpha}{dt} = k(1-\alpha)[-\ln(1-\alpha)]^{n/(n+1)} \quad (1)$$

This is a geometric-probabilistic equation. Within the geometric-probabilistic approach the main co-factors of models have the following interpretation [4]. α is the degree of conversion, the fraction of the original unit reaction space occupied with a new phase. $(1-\alpha)$ is the fraction of the free space. However, another interpretation of this quantity is not less

important, i.e. it determines the interconnection between actual and extended magnitudes $d\alpha/d\alpha_{ext} = 1 - \alpha$ where $-\ln(1 - \alpha) \equiv \alpha_{ext}$ is the extended degree of conversion.

Avrami equation is combined with the n-th order equation

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (2)$$

in which n is 1, 2 or 3. And here we face another essential issue concerning the combination of models. If the interpretation of the co-factor $(1 - \alpha)$ is the same, each of the above values of n deprives it of the meaning of boundary length. And also, values of n obtained for Avrami equation and n-th order equation disagrees considerably. On the other hand, the value of n given in Table 1 for eq. (2) is far from being integer. This implicitly implies a different interpretation for the co-factor $(1 - \alpha)$. But then these two equations cannot be combined into one two-stage model.

Some further relevant issues are illustrated with Table 2. These results have been obtained for the same set of experimental data by different authors.

Table 2. Another set of results for the thermal decomposition of ammonium perchlorate [1]

Models	n	E_a ; kJ mol ⁻¹
1) Avrami equation	$n=2.922 \pm 0.049$	$E_a=99.28 \pm 0.12$
2) n-th order equation OR	$n=0.21 \pm 0.06$	$E_a=111,76 \pm 0.09$
Contracting geometry	$n=1.258 \pm 0.019$;	$E_a=111,76 \pm 0.09$

In addition to equations (1) and (2), contracting geometry equation is used

$$\frac{d\alpha}{dt} = k(1 - \alpha)^{n/(n+1)} \quad (3)$$

where n is 1 for contracting circle and 2 for contracting sphere [5]. The value restored from experimental data is close to $n=1$. Two points are worth note in connection with these results. For the n-th order equation parameters given in Table 2 is close to those given in Table 1, but at the same time parameters found for Avrami equation differ considerably. Even more strange is that contracting geometry equation, completely different by its physical meaning from n-th order equation, gives the same value of efficient activation energy.

This is a good illustration of the current contradiction between direct and inverse problems in solid state reaction kinetics. When direct problems are concerned, the aim is to find some invariants for a process under study, and when different models lead to the same values of parameters, this is a positive result. But from the angle of inverse problems this means that one cannot discriminate such different models as contracting geometry model and n-th order model, and thus the possibility to get an insight into the mechanism is strictly limited.

In some works the Sestak-Berggren equation

$$\frac{d\alpha}{dt} = k\alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p \quad (4)$$

is used with various values of parameters. This generalized model includes the n-th order equation ($m=p=0$), the Prout-Tompkins equation ($m=n=1$; $p=0$), Avrami-Erofeev equation ($m=0$; $n=1$) and some other conventional equations. But when parameters are different, this means some combination of the above equations, and one again faces the problem of interpretation of the co-factors, which may be different in different models and incompatible. If the geometric-probabilistic interpretation is used, it should be taken into account that any choice of $m \neq 1$ negates the fundamental assumption of the equiprobability of nuclei formation [4].

The conclusion is that the above combinations of models, though increasing the approximation flexibility of models, raise a number of essential issues from the angle of inverse problems and require additional discussion. The stages and equations have been selected in the framework of the thermokinetics, and actually the trial-and-error method has been employed which

is becoming more and more inefficient in contemporary chemistry. The issues outlined provide additional weighty arguments in favour of the viewpoint that a further progress in solid state reaction kinetics is hardly possible without passing the limits of thermokinetics towards structural and dynamical considerations.

References

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А.И. Коробов. Обратные задачи гетерогенной химической кинетики: комбинирование простых моделей

Основываясь на результатах масштабного кинетического проекта ICTAC (International Confederation for Thermal Analysis and Calorimetry) "Computational aspects of kinetic analysis", приведено несколько конкретных примеров комбинирования простых термокинетических моделей, приводящего к возникновению проблем, существенных с точки зрения обратных кинетических задач. Эти проблемы не могут быть разрешены в рамках термокинетики и требуют привлечения структурных соображений.