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APPLICABILITY OF ONE-STAGE CHEMICAL REACTION KINETIC EQUATION TO DESCRIBE NON-ISOTHERMAL DESTRUCTION PROCESSES

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The applicability of the traditional kinetic power equation to describe the thermal destruction of solids, and in particular polymers, is discussed. It is shown that in the majority of cases the use of such an equation is reasonable, even though the true mechanism of the process under study is either obscure or so complex that it cannot be analytically described in detail. In such cases the effective rather than the true kinetic parameters are obtained and provide certain useful information on the process.

The fixed conversion temperature dependence on the heating rate is analyzed with examples on the model process and the thermal degradation of an epoxy binder.

In studies on the kinetics and mechanisms of thermal transformations of materials via thermal analysis methods, the well-known kinetic equation is applied:

$$\frac{d\alpha}{d\tau} = Ze^{-E/RT}f(\alpha) \tag{1}$$

where α is the degree of conversion by time τ at temperature T; Z and E are the Arrhenius pre-exponential factor and the activation energy; $f(\alpha)$ is some single-valued function of α, whose form depends on the mechanism of the process. In the case of simple, one-stage chemical reactions, assuming a correct experiment (methodological aspects of non-isothermal experiments are presented in detail in [1]) and a proper choice of the form of the function $f(\alpha)$, Eq. (1) enables one to estimate kinetic parameters which, in the majority of cases, have a distinct physical meaning, using experimental dependences $\alpha(\tau)$ or $\alpha(T)$. If the form of the function $f(\alpha)$ is unknown a priori, as is often the case, then the parameters Z and E may be calculated either from the data of several experiments carried out with different heating rates (for example [2, 3]), or by choosing a function $f(\alpha)$ for which Eq, (1) best fits the experimental function $\alpha(\tau)$ [4]. Wide use is made of the function

$$f(\alpha) = (1 - \alpha)^n \tag{2}$$

where n is the reaction order; this describes the kinetics of homogeneous reactions and heterogeneous processes governed by a phase-boundary reaction mechanism, Eq. (2) being meaningful only for discrete values of n [5].

The thermal decomposition of a solid accompanied by release of a gaseous product, being a heterogeneous process, is usually characterized by a mechanism of nucleation, one- two- or three-dimensional diffusion, etc., and consequently by another form of the function $f(\alpha)$. As some authors correctly note if use is made of the equation

$$\frac{d\alpha}{d\tau} = Ze^{-E/RT}(1-\alpha)^n \tag{3}$$

obtained after substitution of (2) into (1), neglecting the real mechanism of the process, the values of Z, E and n lose their primary physical meaning, and may depend on the degree of conversion and the heating rate, as well as on the experimental conditions in the case of an incorrect experiment [6]. The use of this equation to study composite organic compounds, polymeric and composite materials raises still greater objections [7, 8]. Thermal transformations of such substances are usually a set of very many completely or partially overlapping elementary stages, whose mechanisms, often unknown, may change with varying heating rate, pressure, etc.

Equation (3) has been widely used for many years in thermoanalytical investigations of various classes of materials and transformations. What is the reason for such an adherence to this kinetic equation, which appears to contradict common sense?

First, from a practical point of view a knowledge of qualitative characteristics that allow study and prediction of material properties and behaviour under given conditions is often more important than a detailed elucidation of particular mechanisms of inherent transitions. In other words, if some certainly complex process is sufficiently well described by a one-stage chemical reaction equation of form (3) (referred to be low as a macro-one-stage process), and the true mechanism is obscure or so complex that it cannot be analytically described, this process may be characterized in terms of three "kinetic parameters" using Eq. (3). Under these circumstances, Eq. (3) must be regarded as empirical, and similar to the true kinetic one only in its appearance. The parameters found in this way may depend on the heating rate, which may be presented by the appropriate empirical equations.

It is reasonable to use the empirical equation of form (3) to describe macro-one-stage complex processes for several reasons. This equation can be treated mathematically rather easily, its features being fairly well studied. A great number of exact and approximate methods are known for the calculation of Z, E and n using experimental $\alpha(T)$ and/or $\alpha'(T)$ dependences via Eq. (3). Some of them are so simple that manual calculations may be performed [4]. The kinetic parameters Z, E and n thus obtained may be successfully used to construct mathematical models of the heat treatment of polymer materials, their interaction with high-temperature gas flows, in the production of composite materials with prescribed properties, etc.

It is also important that, even if the true mechanism of the macro-process is inconsistent with Eq. (3), the values of Z, E and n include quite definite useful information on the temperature intervals, intensities and characters of the transformations it describes. Thus, a value of n close to zero denotes the sharp asymmetry of the process, while a high E (or low Z) means that the process is shifted to a high-temperature

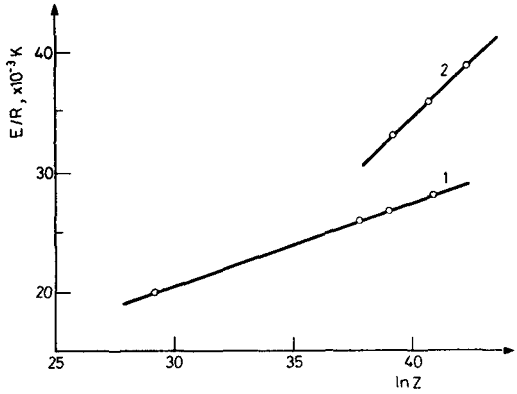

Fig. 1 Compensation dependences for epoxy binders (1) and organic fibres (2). Isokinetic temperatures are 702 ± 15 K and 1018±96 K, respectively

region, etc. In other words, despite a certain formalization, the parameters E and Z retain the meaning of energy and probability (or frequency) characteristics, while n represents the form of the corresponding experimental curves. This enables us to compare the working and technological properties of different materials, the corresponding values of E, Z and n being known from Eq. (3). In contrast to the true kinetic parameters, the latter are reasonably called effective or apparent.

Effective kinetic parameters as a rule obey the laws valid for the true kinetic ones. Our studies have demonstrated the compensation dependence between E and $\ln Z$ obtained via Eq. (3) for the thermal decomposition of some classes of substances similar in structure. In Fig. 1, E/R *vs.* $\ln Z$ is plotted for some epoxy binders and organic fibres. The relative positions of the straight lines shows which of the material classes (in this case fibers) is more heat-stable.

All the above discussion concerning macro-one-stage processes can in general be extended to macro-multistage ones. The calculation of kinetic parameters for separate macro-stages of complex processes characterized by completely or partially overlapping peaks in the function $\alpha'(T)$ is rather tedious, even when the macro-stages are mutually independent [9], but based again on the equation of form (3) used for each stage.

Finally, let us consider one more aspect of the use of Eq. (3) for study of the kinetics of polymer degradation. The authors of [7, 8] criticize the use of Eq. (3) in kinetic calculations, as if it inadequately represents the dynamics of thermal decomposition of polymer materials with increasing heating rate, since it follows from it that with infinitely increasing heating rate, the fixed conversion temperature shifts infinitely to the right, while the experiments they have carried out show that the thermogravimetric curves $\alpha(T)$ tend to approach as the heating rate increases. Hence, they draw the conclusion that some limiting thermogravimetric curve is achieved at some critical heating rate, above which no shift of the process to high-temperature region is observed.

We shall show that Eq. (3), in general, does not contradict the above considerations. Integration of Eq. (3), including some simple transformations, gives an equation uniquely relating the heating rate B and the temperature at which a prescribed degree of conversion α is achieved:

$$B = \frac{Z}{I(\alpha)} \frac{E}{R} p\left(\frac{E}{RT}\right) \tag{4}$$

where $p(E/RT)$ is the exponential integral function tabulated by Doyle [10] (which can be calculated with high accuracy via Schlömilch's expansion) and $I(\alpha)$ is the conversion degree integral:

$$I(\alpha)_{n \neq 1} = \frac{1 - (1 - \alpha)^{1-n}}{1 - n} \tag{4a}$$

$$I(\alpha)_{n=1} = - \ln (1 - \alpha) \tag{4b}$$

Differentiating Eq. (4) with respect to temperature at constant α with allowance for

$$\frac{\mathrm{d}p(E/RT)}{\mathrm{d}T} = \frac{R}{E} e^{-E/RT}$$

gives

$$\left(\frac{\partial B}{\partial T}\right)_\alpha = \frac{Z}{I(\alpha)} e^{-E/RT} \tag{5}$$

As the values of B and T are uniquely related at fixed α, the expression for derivative (5) can be written as:

$$\left(\frac{\partial T}{\partial B}\right)_\alpha = \frac{I(\alpha)}{Z} e^{E/RT} \tag{6}$$

After a second differentiation we obtain:

$$\left(\frac{\partial^2 T}{\partial B^2}\right)_\alpha = - \frac{I(\alpha)}{Z} \frac{E}{RT^2} e^{E/RT} \tag{7}$$

Simultaneous analysis of relations (4), (6) and (7) allows certain qualitative conclusions on the behaviour of $T_\alpha(B)$. This dependence is evidently asymptotic, but the asymptote has a definite (though very small) slope equal to $I(\alpha)/Z$. For $\alpha = 0$ (reaction onset) the asymptote is horizontal. With increasing α the slope of the curves increases somewhat, pointing to expansion of the temperature range with increasing heating rate. The value of this expansion depends on the form of the function $I(\alpha)$, i.e. on the value of the effective reaction order n.

Let us exemplify these conclusions. Figure 2 shows the relation $T_\alpha(B)$ calculated via Eq. (4) for a hypothetical process at $E/R = 30000$ K, $Z = 10^{20}$ min^{-1}, $n = 0$ (a)

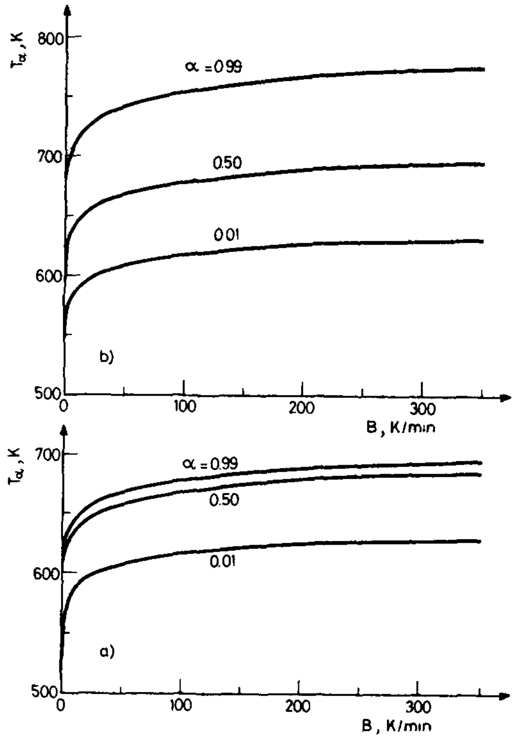

Fig. 2 *Temperature of fixed degree of conversion vs. heating rate at $E/R = 30000$ K, $Z = 10^{20}$ min^{-1}, $n = 0$ (a) and $n = 2$ (b)*

and $n = 2$ (b). It is seen that the effect of a heating rate increase on T_α is essential only at small B (up to 30 deg/min). At heating rates above 200 deg/min the effect is rather insignificant. Taking into account that, with rapid heating, the real increase of the sample temperature inevitably lags behind the prescribed value and the error in the temperature measurements increases, the confluence of the thermogravimetric curves can easily be explained.

Figure 3 plots $T_\alpha(B)$ for three values of α obtained experimentally by the present authors in a study of the thermal decomposition of an epoxy binder on a Perkin–Elmer TGS-1 instrumnet at heating rates from 5 to 160 deg/min. These coincide qualitatively with the relationships in Fig. 2.

Thus, the analysis provides good grounds to conclude that, if the used experimental data are correct, Eq. (3) is quite valid for describing complex processes such as the thermal decomposition of polymer materials, and enables one to obtain effective kinetic parameters of practical importance.

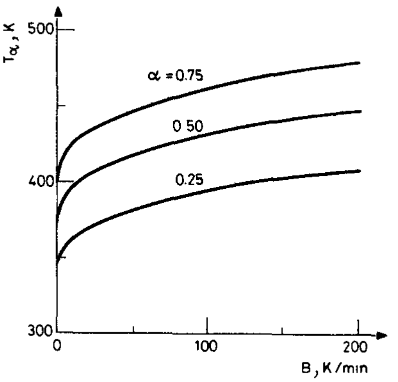

Fig. 3 Temperature of the fixed degree of conversion for an epoxy binder *vs.* heating rate

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Zusammenfassung — Die Anwendbarkeit der traditionellen kinetischen Energie-Gleichungen zum Beschreiben der thermalen Zersetzung von festen Materialien, und besonders von Polymeren, wurde besprochen. Es wurde gezeigt, dass die Anwendung einer solchen Gleichung in den meissten Fällen begründet ist, auch wenn das wahre Mechanismus des untersuchten Vorganges entweder unklar, oder so zusammengesetzt ist, dass es sich analytisch nicht beschrieben lässt. In solchen Fällen werden eher die effektiven als die wahren Parameter erhalten, und geben gewisse brauchbare Informationen über den Vorgang.

Die bestimmte Abhängigkeit der Umwandlungstemperatur von der Erwärmungsgeschwindigkeit wurde durch Beispiele an dem Modellvorgang, und dem thermischen Abbau eines Epoxy-Bindematerials analysiert.

Резюме — Обсуждается применимость традиционного степенного кинетического уравнения для описания термодеструкции твердых веществ и, в частности, полимеров. Показано, что в большинстве случаев использование такого уравнения целесообразно, даже если истинный механизм исследуемого процесса неясен или настолько сложен, что не может быть детально описан аналитически. Получаемые при этом эффективные кинетические параметры несут вполне определенную полезную информацию о процессе. На примерах модельного процесса и термического разложения эпоксидного связующего проанализирована зависимость температуры фиксированной степени превращения от скорости нагрева.