Journal of Thermal Analysis, Vol. 12 (1977) 179—185

MATHEMATICAL MODELLING OF THERMAL DECOMPOSITION PROCESSES

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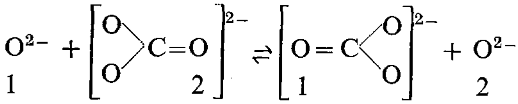
(Received February 26, 1977)

Some possible elementary reactions are not included in the classical mathematical models of thermal decomposition. For example, we can assume that in the thermal decompositions of simple carbonates a proportion of the O^{2-} ions produced on the reaction interface can migrate into the interior of the reactant phase, since at this temperature there is some probability of CO_2 exchange between an O^{2-} and a neighbouring CO_3^{2-} ion. A similar diffusion-type process can be assumed in a wide class of decomposition reactions. The present state of computer science makes it possible to show by mathematical modelling how this migration influences the TG curves of the simplest contracting-sphere-type reactions. The resulting extended contracting-sphere model can provide the induction and the acceleration period of the TG curves.

It is well known that several elementary processes take place even in the simplest thermal decomposition reactions of type

$$A_{solid} \rightarrow B_{solid} + G_{gas} \qquad (1)$$

Since these reactions form the basis of thermogravimetric analysis, it would be useful if, even by approximative mathematical models, one could show how the different elementary processes influence the TG curves. Though a great number of mathematical models exist in the literature on thermal analysis [1, 2], they do not take into account all possible physical or chemical elementary processes. Let us consider, e. g., the decomposition of a carbonate, when O^{2-} ions are produced at the reaction interface. At the temperature of the thermal decomposition the following exchange reaction can take place between an O^{2-} ion and a neighbouring CO_3^{2-} ion:



(2)

It should be noted that the cations, having small dimensions, cannot represent significant geometrical hindrances, and the energy barrier of the above CO_2 jump is probably smaller than the energy necessary for the decomposition of a CO_3^{2-} ion. In this way one can assume that a considerable proportion of the O^{2-} ions produced on the reaction interface appear in the still unreacted part of the decomposing material. Formally, this process is analogous to vacancy-type diffusion in solids. Similar diffusion-type processes may take place in a wide class of thermal decompositions and can significantly affect the rate of advance of the reaction interface.

The purpose of the present work is to show the effects of this diffusion-type process in the case when the reaction interface appears on the external surface of the particle and advances from the exterior to the interior. In other words: we extend the classical contracting-sphere model by including the above diffusion processes. We shall use equations based on physical and chemical evidence to describe the advance of the reaction interface and the decrease in the amount of undecomposed material. The equations have been solved by a computer for some sets of parameters to show that the presented model can provide the induction period and the acceleration period of the TG curves. The corresponding numerical method is outlined briefly in the Appendix.

Mechanism and elementary processes

Since we should like to show as clearly as possible the effects of the diffusion-like processes outlined above, we attempt to reduce the number of other factors by treating only those decomposition reactions which

i) from a chemical point of view are simple one-step reactions;

ii) may be characterized by the fact that the product phase appears first at the external surface of the particle and the reaction interface advances from the exterior to the interior;

iii) have a smaller product molecular volume than that of the reactant;

iv) are examined in vacuum and the sample investigated consists of small particles.

Note that condition ii) is the basic assumption of all contracting-sphere or shrinking-core-type models. Condition iii) is statisfied by the majority of thermal decomposition reactions [1]. Conditions iii) and iv) are necessary to rule out diffusion control; otherwise, the product phase and the gas layer retained in it would represent a considerable resistance for the stream of molecules of gas *G*.

First of all, let us examine the decomposition of a single particle of spherical shape. To simplify the treatment, let us divide the particle into hypothetical thin concentric layers. The following elementary processes will be considered:

1. Molecules of gas *G* can leave the outermost layer and pass directly into the vacuum. Here a unimolecular surface reaction is assumed.

2. Those sites in the reactant phase, from which the molecules of *G* are absent, will be denoted by *V* in the following. In dehydration processes, for example, a site *V* corresponds to a real vacancy of a H_2O molecule, whereas in the case of carbonate decomposition, *V* is an O^{2-} occupying the place of a CO_3^{2-} ion. We assume, as mentioned above, that a certain proportion of the sites *V* migrate from

the reaction interface into the reactant phase, since molecules of G bound in any form at the neighbouring lattice sites of the reactant phase can jump into them with a certain probability.

3. As a consequence of the above two processes, the mole fraction of undecomposed material decreases most rapidly in the outermost thin layer of the reactant phase. When it achieves a certain critical value here, which will be denoted by c_{rupt}, the crystal structure of the reactant phase does not tolerate the quantity of sites V any longer, and the separation of the product phase from the reactant phase begins here. The product phase having a smaller molecular volume than the reactant (assumption iii)), this process produces different forms of diffusion short-circuits and other irregularities in this layer, markedly speeding up the decomposition here. To obtain a simple mathematical model for the phenomena, it is supposed that if the mole fraction of undecomposed material reaches this critical c_{rupt} value in the outermost thin layer of the reactant phase, this layer will decompose instantly.

4. As a consequence of assumptions iii) and iv), the decomposed layer does not represent a significant resistance to the stream of the molecules of gas G evolved now in the lower layers, so these molecules can now pass out into the vacuum from the external surface of the next layer. When the mole fraction of undecomposed material decreases below the critical c_{rupt} value here again, this layer is also assumed to decompose instantly. This mechanism continues step by step until the decomposition of the whole particle is accomplished.

Mathematical model

Let us denote the molar concentration of the undecomposed material at a given point of the reactant phase by c, which will be a function of time t and (in particles having spherical symmetry) will also depend on the distance from the centre. If this latter is denoted by r, c may be written as $c = c(r, t)$. Its initial value will be denoted by c_0. Let R_i $(i = 0, 1, 2, \ldots)$ be the actual radius of the reactant phase region. The rate per unit area of the surface reaction (v_s) will be described by the expression

$$v_s = k\, c(R_i, t) \tag{3}$$

where k is the corresponding specific rate constant. The migration of sites V in the reactant phase will be described by Fick's laws. The constant D appearing in Fick's laws has the same meaning here as in the case of the diffusion of real vacancies, i.e. D is a quantity proportional to the probability of jumping into a site V. The molar concentration of sites V in the reactant phase is $c_0 - c$. Fick's first law gives the flux per unit area of sites V (v_D):

$$v_D = -D \operatorname{grad}(c_0 - c) \tag{4}$$

Since sites V are produced by the evolution of molecules of G at the boundary of the reactant phase, $v_s + v_D$ must be zero here:

$$k\, c(R_i, t) - D\,[\operatorname{grad} \mathrm{c}_0 - c(R_i, t)] = 0 \tag{5}$$

Fick's second law gives an equation for the distribution of sites V in the interior of the reactant phase:

$$\frac{\partial(c_0-c)}{\partial t} = D\nabla^2(c_0 - c) \tag{6}$$

Note that Eqs (5) and (6) correspond to a boundary problem frequently used in the theory of heat conductivity. Theoretically, the mathematical model corresponding to the mechanism outlined in the previous section is now ready: one could solve Eqs (5) and (6) by placing the boundary at R_0 up to t when $c(R_0, t)$ achieves c_{rupt}, and continue the solution by placing the boundary at R_1 up to t when $c(R_1, t)$ achieves c_{rupt} and so on. When the boundary is at R_0, the initial condition is $c(r, 0) = c_0$.

However, as regards the thickness of the hypothetical thin layers, it must be noted that they should have very small dimensions. This means that this simple computational scheme would consist of a very great number of steps. Therefore, we need some practical approximation. The simplest way seems to be to assume the thickness of the hypothetical thin layers to be infinitesimally small, i.e. to use the limit $h_i = R_{i-1} - R_i \to 0$.

In this way the computations can be carried out without any difficulties, as is briefly outlined in the Appendix.

Calculated TG curves

The outlined mathematical model contains the following four parameters: k, D, c_{rupt} and R_0, the initial radius of the particle. In order to have a general view of the character of the calculated TG curves, the units of time and length may

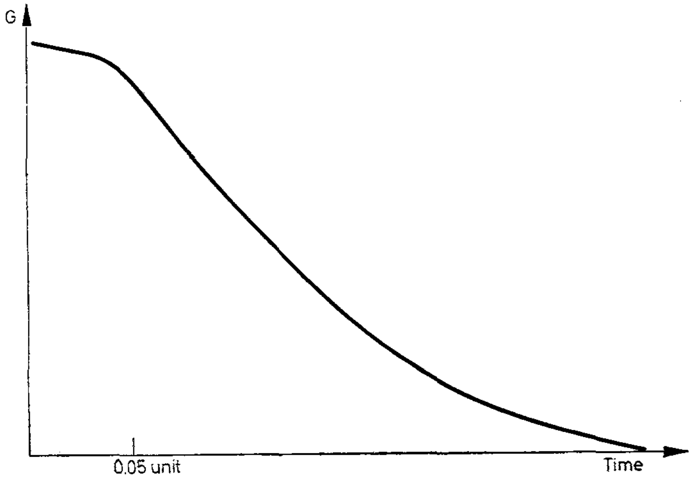


Fig. 1. Simulated TG curve at $k = 1$, $R_0 = 1$, $c_{\text{rupt}} = 0.8$ and $D = 0.25$

be chosen arbitrarily. In other words: we may choose units for time and length such that the values of R_0 and k will be one. To study the dependence of the calculated TG curves on the remaining two parameters (D and c_{rupt}) we have carried out many example calculations. In a wide domain of D values we obtain TG curves having induction and acceleration periods. Some of them are shown in the Figures.

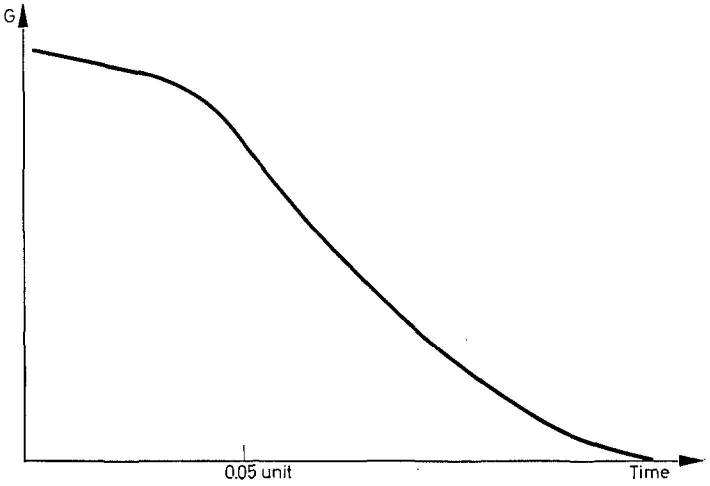


Fig. 2. Simulated TG curve at $k = 1$, $R_0 = 1$, $c_{\mathrm{rupt}} = 0.8$ and $D = 1$

Fig. 3. Simulated TG curve at $k = 1$, $R_0 = 1$, $c_{\mathrm{rupt}} = 0.8$ and $D = 4$

Possibilities of further development of the model

The present state of computer science would permit the developing and computing of more complicated mathematical models too. Among others, one could apply the present mechanism scheme to non-spherical, non-isotropic crystals. It is possible to derive TG curves for samples having non-uniform particle size, and it is no problem to estimate the unknown parameters of the model via the least squares approximation of measured TG curves. However, we should like to point out that at the time being we do not have the necessary information on the physics and chemistry of thermal decompositions to develop mathematical models without simplifications and approximative terms. This means that for the time being the aim of the mathematical modelling of the elementary process of thermal decomposition can be only to understand the observed TG curves and at most to estimate the significance and magnitudes of the different elementary processes.

Appendix: numerical solution

Let us write Eqs (5) and (6) in the identical simpler form:

$$k\,c(R_i, t) + D \operatorname{grad} c(R_i, t) = 0 \tag{7}$$

$$\frac{\partial c}{\partial t} = D\nabla^2 c \tag{8}$$

In polar coordinate system the operator ∇^2 has a rather complicated form but as can be found in the textbooks, if central symmetry exists, Eq. (8) can be written in the following simple form:

$$\frac{\partial (rc)}{\partial t} = D\frac{\partial^2 (rc)}{\partial r^2} \tag{9}$$

Assuming $h \to 0$, we shall have the following moving boundary problem: "after c has reached the value c_{rupt} at the boundary, the position of the boundary, R, begins to diminish in such a way that the relation

$$c(R, t) = c_{\mathrm{rupt}} \tag{10}$$

should stand". In other words: we look for those functions $c(r, t)$ and $R(t)$ for which Eqs (7), (8) and (9) hold. This problem is a special case of Stephan's problem [3]. The numerical solution of a similar problem is treated by Ehrlich [4]. His method can be applied here without any significant change. The main points of the method are the following:

As in the case of all finite difference solutions, we compute the values of the unknown functions $c(r, t)$ and $R(t)$ only at some discrete points r_i and t_j. We replace the differential quotients by difference quotients. In this way a system of linear algebraic equations is obtained which is easy to solve. The finite difference analogues of Eqs (7), (9) and (10) are well known or trivial. We use equidistant points ($r_i - r_{i-1} = \delta r$) and choose them in such a way that R_0 should be at the centre of a distance δr. In the moving boundary period of the decomposition we choose t_j values such that $R(t_{j+1}) - R(t_j)$ should be about δr, and $R(t_j)$ should be near to the centre of a difference dr. In our opinion the simplest way to choose such t_i values is the application of the forward difference analogue of Eq. (9), while the final $c_{j,i}$ values are computed by the more precise Crank–Nicolson formulae.

References

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RÉSUMÉ — Quelques réactions élémentaires possibles ne sont pas prises en compte dans le modèle mathématique classique de la décomposition thermique. On peut, par ex., supposer que lors de la décomposition thermique des carbonates simples, une partie des ions O^{2-} formés à l'interface de réaction puisse migrer à l'intérieur de la phase réagissante, puisqu'à cette température il existe une certaine probabilité d'échange entre un O^{2-} et un ion CO_3^{2-} voisin. On peut supposer un processus similaire du type diffusionnel chez un grand nombre de réactions de décomposition. L'état actuel de la science des ordinateurs permet de montrer, à partir de modèles mathématiques, l'influence de cette migration sur les courbes TG des réactions les plus simples du type sphères de contraction. L'extension du modèle des sphères de contraction peut indiquer les périodes d'induction et d'accélération sur les courbes TG.

ZUSAMMENFASSUNG — Einige mögliche Elementarreaktionen sind in dem klassischen mathematischen Modell der thermischen Zersetzung nicht enthalten. Z. B. kann angenommen werden, daß bei der thermischen Zersetzung einfacher Carbonate ein Teil der an der Reaktionsgrenzschicht entstandenen O^{2-}-Ionen in das Innere der reagierenden Phase wandern kann, da bei dieser Temperatur eine gewisse Wahrscheinlichkeit eines CO_2-Austausches zwischen einem O^{2-} und einem benachbarten CO_3^{2-}-Ion besteht. Ein ähnlicher Vorgang vom Diffussionstyp kann bei einer großen Gruppe von Zersetzungsreaktionen angenommen werden. Die gegenwärtige Lage der Komputerwissenschaft ermöglicht an Hand der mathematischen Modellierung den Einfluß dieser Wanderung auf die TG-Kurven der einfachsten Reaktionen vom Typ der Kontraktionssphären zu zeigen. Das erhaltene erweiterte Kontraktionssphären-Modell kann die Induktions- und Beschleunigungsabschnitte der TG-Kurven liefern.

Резюме — В классических математических моделях термического разложения не содержались некоторые возможные элементарные реакции. Так, например, можно допустить, что при термическом разложении простых карбонатов часть O^{2-} ионов, образующихся на реакционной поверхности раздела, может мигрировать внутрь реагирующей фазы, поскольку при этой температуре имеется некоторая возможность обмена CO_2 между O^{2-} и соседним CO_3^{2-} ионом. Можно допускать, что подобный диффузионный процесс возможен в широком классе реакций разложения. Современный уровень вычислительной техники позволяет показать с помощью математического моделирования каким образом такая миграция оказывает влияние на кривые ТГ простейших типов реакций с сжимаемой сферой. Такая модель результирующей расширенно-сжимаемой сферы может давать индукционный период и период ускорения кривых ТГ.