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THERMOKINETIC COMPARTMENT MODELS OF THERMAL DECOMPOSITION REACTIONS

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ABSTRACT

The use of tank reactor (CSTR) type mathematical models is proposed for describing the mean internal regimes (reaction zones) of decomposition processes and to relate them to TGA plots which exhibit a normal sigmoid, or some particular oscillating overall rate. The ordinary differential equations of these models can be solved by standard numerical procedures for initial value problems. As an example for the description of normal decompositions, a CSTR model is discussed which refers to a simple elementary reaction of arbitrary order. The multistability of this model may explain the occurrence of different decomposition regimes which had been measured for kaolin and for limestone.

INTRODUCTION

In order to describe phenomenologically the internal regime, and the concentration profiles of decomposition processes with oscillating rates [1,2], different systems of partial differential equations (PDEs) have been proposed [3,4]. Of course, these equations can also be used to describe quasistationary processes leading to normal sigmoid overall rates exhibited in many TGA plots. Here, an approach is developed which uses a compartment description of the samples and bases on systems of ordinary differential equations (ODEs). Mathematical models of this type are similar to the thermodynamics of irreversible processes in discontinuous systems [5,6], and the theory of chemical reactors [7,8]. Their basis is to take the reaction zones, i.e. reactive phase boundaries, or sections of them, as the bulk of homogeneous tank reactors (CSTRs).

This procedure seems very promising from both theoretical and practical points of view. To see this, one should take into consideration that compartment models including CSTRs can well be adapted to various situations, and that the computational techniques for solving dynamic problems of nonlinear ODEs is much more developed than for solving problems of nonlinear PDEs.

The most general model of the compartment type would be a cascade of coupled homogeneous tank reactors. The ODE systems of such CSTRs systems can have many qualitatively different sets of solutions (trajectories)

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describing the time evolution of processes. This fact provides a number of different aspects to the explanation of thermal decomposition reactions. If it is assumed that a compartment modelling is correct, then, except for the above mentioned processes with self-oscillating rates, even chaotic variations of rates could be expected as another possible result of TGA measurements. Quasistationary states of the CSTR models which slowly vary with time would have to be connected with the normal decomposition reactions leading to sigmoid overall gas evolution curves. In this line, the multistability of the CSTR models comes into play.

This is the very topic which we will pick up in the following. The occurrence of different steady states of a rather simple tank reactor model shall be related with some results of measurement [1] for the decomposition of kaolin, and of limestone.

TANK REACTOR MODEL WITH ONE REACTION OF ARBITRARY ORDER

The elementary mechanism

$$nA_{sol} \xrightarrow{k} mC_{sol} + lW_{gas} \tag{1}$$

(where n, m, l are non-negative integers) might be interesting for many decomposition reactions. Let us assume that a zone, or interface, in which the reaction (1) proceeds, is running from the outside into a crystal of pure initial substance A. We regard a part of the reactive region which is cut out by a thin cylinder pointing from the center of the sample to its surface.

This section of the reaction region may directly be identified with the bulk of a tank reactor (cf. Fig. 1). In some cases, the region corresponding to the bulk of the tank might also reach up to the surface of the sample. At exterior heating, the section of the reaction region will be supplied with an integral heat flux I_Q. By the motion of the tank towards the center of the crystal, a convective flux I_A of fresh substance A into the tank will occur, and fluxes I_C and I_W, of C or W, will stream out. The flux I_W is not purely convective. It will contain a contribution due to outward diffusion of W.

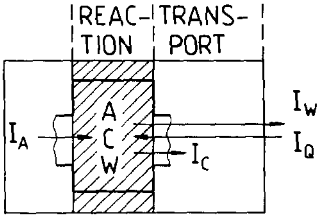

Fig. 1. Scheme of modelling of decomposition processes. A section of the reaction zone (or surface) is regarded as a tank reactor with a homogenous bulk (CSTR) which moves through the sample. I_A, I_C and I_W are the flows of components, A, C and W; I_Q is the flow of heat.

Another way of interpreting a CSTR model in which reaction (1) proceeds is to take it in a transposed, or symbolic meaning for the overall transformation occurring in a spatially closed two-fold connected 3-dimensional reaction region, or for the transformation on a closed 2-dimensional reaction surface. In either case of interpretation, the ODEs of the CSTR model with the elementary reaction (1) may be written in the form

$$\begin{aligned} \dot{a} &= -nka^n + J_A \\ \dot{c} &= mka^n - J_C \\ \dot{w} &= lka^n - J_W \\ c_p\dot{T} &= nka^n\Delta h + J_Q \end{aligned} \tag{2}$$

Here a, c and w are particle number densities per unit volume (mol cm^{-3}), or per unit surface (mol cm^{-2}) of the components A, C and W, respectively, and T is the temperature. The heat capacity of the unity reaction region is denoted as c_p, and Δh is the molar reaction enthalpy of eqn. (1). The Arrhenius ansatz

$$k = z\,\mathrm{e}^{-E/RT} \tag{3}$$

shall be assumed for the temperature dependence of the rate coefficient k. The dot $(\cdot)$ denotes the time derivative $(\cdot) \equiv \mathrm{d}/\mathrm{d}t$. The quantities J_S (S=A, C, W or Q) are the yield of the flows I_S of components A, C and W, and of heat per unit volume, or per unit surface, respectively, in the reaction region, i.e.

$$J_S \equiv I_S/V \quad (\mathrm{mol\ cm^{-3}\ s^{-1}}) \quad \text{or} \quad J_S \equiv I_S/F \quad (\mathrm{mol\ cm^{-2}\ s^{-1}}) \tag{4}$$

The J_S are functions of the state variables a, c, w and T. These functions must be chosen in correspondence with the mean local conditions in the reaction zone, and with its boundary conditions, and obviously depend on the special interpretation of the reactor model.

Expressions for J_S can be obtained, if one assumes that some profiles of the state variables are known as solutions of the corresponding PDE problem at special boundary conditions. The CSTR equations can then be defined by averaging the various terms of the PDEs on the space variable ζ through the reaction zone (see for example refs. 3 and 4). For instance, if a section of a constantly progressing reaction zone with step-like profiles similar to the profiles in Fig. 2 are described by a tank like that in Fig. 1, then the following equations can be used:

$$J_A = Na_0 \qquad J_C = Lc_f \tag{5}$$

$$J_W = M(w - \mu w_e) \qquad J_Q = K(T_e - T) \tag{6}$$

In this ansatz, the constant initial volume density a_0 of the crystal of pure A, and the constant final density c_f of the produced structure of C are introduced. The constants N and L depend on the velocity v of the reaction

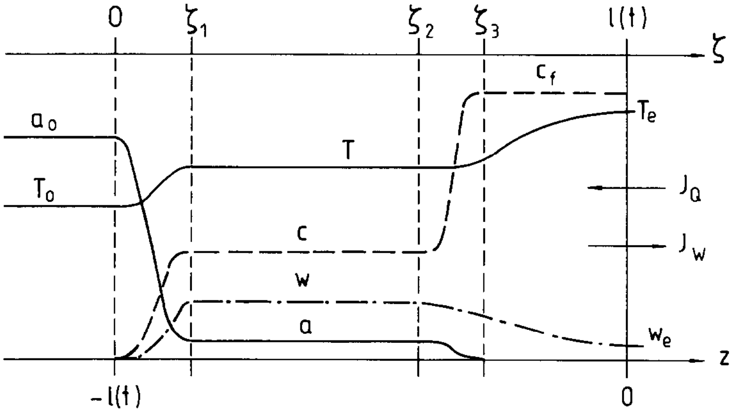

Fig. 2. An example of concentration and temperature profiles along a coordinate axis z (or ζ) pointing from the center of the crystal to its outer surface. This case conveniently allows to deduce the ODEs of a CSTR model from corresponding PDEs. J_Q and J_W, diffusion flows of heat and gas through unit cross section of the exterior surface of the sample, respectively.

zone, and of its thickness $\Delta\zeta$, viz. $N = L = v/\Delta\zeta$. The constants M and K, respectively, are transition numbers for the diffusion of W, and the conduction of heat between the reaction zone and the surroundings of the crystal. In the surroundings, the values of the nonvanishing state variables w and T are w_e and T_e. The coefficient μ characterizes the equilibrium particle distribution of W at the exterior surface of the crystalline substance C.

If the steps of the profiles of the reaction zone should extend from the interior reaction front out to the exterior surface of the sample, the eqns. (5) would have to be substituted by

$$J_A = N(a_0 - a) \qquad J_C = 0 \tag{7}$$

Another possibility for defining the flow rates J_A and J_C would be to assume that the particle number densities a and c in the tank reactor had stationary values $a = \text{const}$ and $c = \text{const}$. Then, the vanishing of the left hand sides of the first two rate equations (2) would prescribe expressions for J_A and J_C as functions of T (cf. eqn. 3).

DISCUSSION OF A SPECIAL CASE OF THE ODES

Using the assumption of eqns. (3), (6) and (7), the ODEs (2) obtain a special form in which they contain

$$\begin{aligned} \dot{a} &= -nze^{-E/RT}a^n + N(a_0 - a) \\ c_p\dot{T} &= nze^{-E/RT}a^n\Delta h + K(T_e - T) \end{aligned} \tag{8}$$

as the only simultaneous subsystem. After numerical computation of solutions $a = a(t)$ and $T = T(t)$ of eqns. (8) at given parameter values and given initial conditions, the functions $c = c(t)$ and $w = w(t)$ can be obtained from eqns. (2) by computation of integrals.

For these computations, a transition to dimensionless quantities is useful, e.g., $\beta \equiv \Delta h R a_0/c_p E$, $\gamma \equiv K/nc_p z a_0^{n-1}$, $\nu \equiv N/nza_0^{n-1}$, $\xi \equiv a/a_0$, $\vartheta \equiv RT/E$, $t' \equiv nza_0^{n-1}t$, $(') \equiv \mathrm{d}/\mathrm{d}t'$. This leads from eqn. (8) to

$$\begin{aligned} \xi' &= -\xi^n \mathrm{e}^{-1/\vartheta} + \nu(1-\xi) \equiv f_\xi \\ \vartheta' &= \beta \xi^n \mathrm{e}^{-1/\vartheta} + \gamma(\vartheta_e - \vartheta) \equiv f_\vartheta \end{aligned} \tag{9}$$

We ask for trajectories of eqns. (9) with $\xi = \xi\,(t') > 0$ and $\vartheta = \vartheta(t') > 0$ at parameter values $\vartheta_e > 0$, $\nu > 0$ and $\gamma > 0$. If the normal case of a simple endothermic decomposition shall be described, we have $\beta < 0$, and if an exothermic reaction step is to be regarded then the condition is $\beta > 0$. First, the steady states (ξ_s, ϑ_s) in the positive region of the phase plane of eqns. (9) shall be investigated. The definition $f_\xi = f_\vartheta = 0$ of these singular trajectories leads to

$$\gamma(\vartheta_e - \vartheta) = -\beta\left[1 + \frac{\gamma}{\beta\nu}(\vartheta_e - \vartheta)\right]^n \mathrm{e}^{-1/\vartheta} \equiv F(\vartheta) \tag{10}$$

Solutions of eqn. (10) may be obtained by graphical discussion.

Figure 3 illustrates schematically the endothermic case $\beta < 0$. The straight line which characterizes the heat transport has a negative slope. Consequently if n is odd only one steady state will exist, but if n is even, three

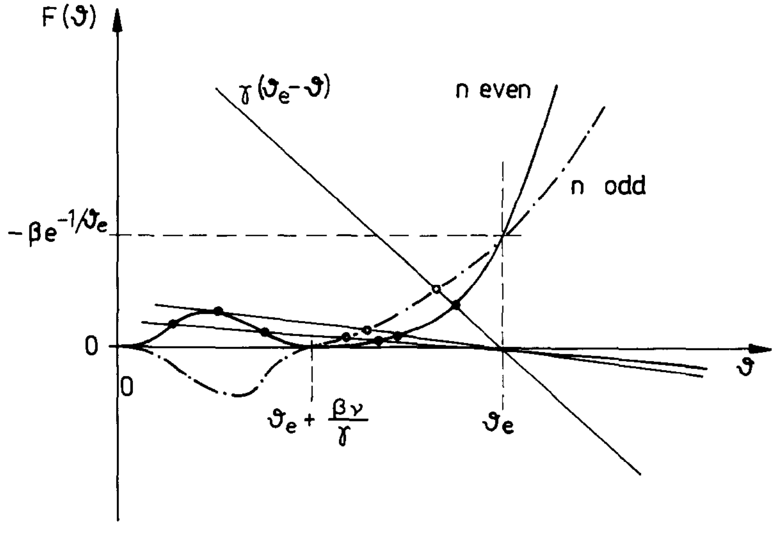

Fig. 3. Schematic diagram of the graphic solution of eqn. (10) at positive ν, γ and ϑ_e and negative β.

singular points might occur. Since structural stability of the model has to be demanded (see [9,10]), the parameter values with two steady states must be excluded. At $\beta < 0$, each steady state (ξ_s, ϑ_s) in the region $\xi > 0$ fulfils the Hurwitz stability condition (see [9,10]).

In the exothermic case, $\beta > 0$, the graphic solution of eqn. (10) is similar to that shown in Fig. 3. A picture for $n = 1$ has already been presented in ref. 11 (example 1.9.1). In this case, three steady states may occur not only when n is even, but also when n is odd.

Second, we ask for self-oscillating solutions $\xi = \xi(t')$ and $\vartheta = \vartheta(t')$ of eqns. (9). Their existence can be excluded, if $\beta < 0$. This follows by application of the Bendixon negative criterion (see, for example [9,10]). In the exothermic case, $\beta > 0$, limit cycles of eqns. (9) exist at special parameter values as show by various investigations (e.g. refs. 12 and 13). These papers use a slightly different dimensionless form of eqns. (8) for $n = 1$. They include examples of numerical computation of self-oscillating trajectories.

APPLICATIONS TO SOME DECOMPOSITION REACTIONS

Measurements of the dependence of the temperature, T_m, of the maximum overall decomposition rate on the sphere diameter, $\mathscr{L}$, of samples of kaolin and limestone [1], (see Figs. 2 and 4 and Tables 2 and 3 in ref. 1) have indicated two different branches of $T_m - \mathscr{L}$ plots. At large diameters, $\mathscr{L}$, these results show that the values of T_m are disproportionally large when compared with the values of T_m resulting with smaller samples.

For an explanation of this fact, the multistable special case of our model (2) which is given by eqns. (8) with $\beta < 0$, and with bimolecular collisions $n = 2$ seems to be appropriate. It is seen that the heat transition number K, or γ, of the effective reaction zone of small samples is much greater than that of larger samples. At high values of γ, the straight line of Fig. 3 becomes very steep, and a steady state which can approximate a quasi-stationary decomposition process will have a high temperature $\vartheta = \vartheta_s$. On the other hand, at small values of γ at which three steady states may occur, the decomposition process can go on at the steady state with the smallest value $\vartheta = \vartheta_s$. For intermediate sizes of samples, a bifurcation via the above mentioned structurally unstable regime of the degenerate case with two steady states has to be expected. This bifurcation explains the gap of the $T_m - \mathscr{L}$ measurements in ref. 1.

At first sight, the self-oscillating solutions of the model (eqns. 2) with eqns. (3,5,7) based on the reaction (1) seem also to be applicable to an explanation of the oscillations of the overall rate at the decomposition of gypsum (see ref. 1, Fig. 5, or its corrected copy in ref. 3). One might suppose, for example, that eqns. (9) refer to an appropriately chosen single step of the elementary reactions which had been proposed in ref. 4. However, we must observe that the only exothermic step of these elementary mechanisms is $2CaSO_4 + H_2O \rightarrow 2CaSO_4 \cdot 1/2\ H_2O$. This equation cannot, however, be identified with (1) even if the symbols are renamed. Consequently, the model (eqns. 2) with eqns. (3), (5) and (7) is inapplicable to the description of the oscillations in Fig. 5 of ref. 1.

CONCLUSIONS

The consideration of a special case of ODEs has indicated that the model (eqns. 2) with $n = 2$ may be adopted to describe the decomposition of kaolin and of limestone [1]. This supports the conclusion that these two decompositions proceed by second order collisions. Since our model proved to be inapplicable to oscillating endothermic reactions, we must conclude that the decomposition of gypsum ([1], Fig. 5) cannot proceed via a simple elementary mechanism of the type (1).

These statements are purely qualitative. However, the purpose of the method using CSTR models is not only to provide qualitative explanations of decomposition reactions, but also to give a quantitative description of them. Of course, this would require one to say which interpretation of the model should be chosen, and to include exact information on the geometric and other data in the modelling. Furthermore, the time evolution of trajectories of the ODEs of the model would have to be investigated numerically. In doing this it must be observed that the trajectories depend on data such as initial crystal dimensions, initial crystal state, transport coefficients, rate coefficients, and heating rates. These data are involved in the initial conditions, in values of the parameters, and, from a strict point of view, even in time dependent functions appearing in the ODEs.

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