

THERMOKINETIC MATHEMATICAL MODEL OF THE REACTION ZONE OF AN OSCILLATING THERMAL DECOMPOSITION REACTION

HANS STROBEL

*Sektion Physik, Friedrich-Schiller-Universität, DDR-6900 Jena,
Max-Wien-Platz 1 (G.D.R.)*

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ABSTRACT

A reaction–diffusion type system of partial differential equations is proposed for the description of an oscillating decomposition regime of gypsum which has been indicated by thermogravimetric measurements by Heide et al. (1980). A discussion of the model shows that the observed oscillations of the stream of evading water vapor may be caused by the onset of self-oscillations, and the formation of structures, of thermokinetic origin. The exothermic heat effect of the back reaction of water into hemihydrate proves to be an essential precondition of the oscillations. Oscillations of quasi-isothermal chemical type are rather unlikely.

INTRODUCTION

A paper by Heide, Kluge and Hlawatsch [1] reports that the thermal decomposition of medium-sized (36.1–50.5 mg) samples of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is attended by an oscillating stream of water vapor. Here, we propose a phenomenological description of these decomposition reactions by a system of partial differential equations (PDEs). The description assumes that the onset of oscillations is due to thermokinetic nonlinearities. Physical aspects of an approximative separation of this system of PDEs will be discussed.

The current level of experimental knowledge of the interior mechanism of the decomposition is rather low. This justifies our mathematical discussion of the given PDEs aiming only at a preliminary estimate of various possible explanations of the experiment on the basis of the given model. Other possible models have been discussed in an earlier paper developing a quasi-isothermal semi-kinetic approach [2].

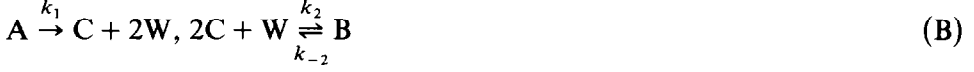
BASIC EQUATIONS

Gypsum and its decomposition products will be denoted by $A \equiv \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $B \equiv 2\text{CaSO}_4 \cdot \text{H}_2\text{O}$, $C \equiv \text{CaSO}_4$, $W \equiv \text{H}_2\text{O}$. The different crystalline mod-

ifications of the hemihydrate B shall not be distinguished. The two consecutive reactions



or



shall be assumed to be different possible elementary reactions of the decomposition. Experimental data on the single steps of the mechanism (A) or (B) may be found in refs. 3 and 4, or in the papers quoted therein.

The kinetics of the decomposition will be described by a 1-dimensional model. We assume the existence of a continuous reaction zone of the sample which is preceded by an interior phase boundary discontinuity. The origin $\zeta = 0$ of a rigid axis of coordinates $\{\zeta\}$ shall be fixed to this discontinuity as a point of reference. The ζ -axis is supposed to be parallel with the outward normal of the crystal surface.

The velocities v_A, v_B, v_C of the components A, B, C with respect to the system $\{\zeta\}$ are assumed to agree with the local velocity v_L of the lattice of the crystal, i.e., $v_A = v_B = v_C = v_L(\zeta, t)$. A nonvanishing diffusion flux of water W, and the heat flux will be taken into account. The diffusion coefficient and the heat conduction coefficient will be denoted as D and λ , respectively.

With these suppositions, the system of balances of particle number and of enthalpy (of the density $h = c_p T + \text{const}$) may be written as

$$\begin{aligned} \partial_t a + \partial_\zeta (a v_L) &= f_A \\ \partial_t b + \partial_\zeta (b v_L) &= f_B \\ \partial_t c + \partial_\zeta (c v_L) &= f_C \\ \partial_t w + \partial_\zeta (w v_L) - \partial_\zeta (D \partial_\zeta w) &= f_W \\ \partial_t T + \partial_\zeta (T v_L) - \partial_\zeta^2 T &= f_T \end{aligned} \quad (1)$$

where the rate functions according to the kinetics (A) or (B), respectively, are

$$\begin{aligned} f_A &= -2k_1 a^2, f_B = k_1 a^2 + k_{-2} c^2 w - k_2 b, f_C = 2k_2 b - 2k_{-2} c^2 w, \\ f_W &= 3k_1 a^2 + k_2 b - k_{-2} c^2 w, f_T = \frac{1}{c_p} [2k_1 a^2 \Delta h_1 + (k_2 b - k_{-2} c^2 w) \Delta h_2] \end{aligned} \quad (1A)$$

or

$$\begin{aligned} f_A &= -k_1 a, f_B = k_2 w c^2 - k_{-2} b, f_C = k_1 a - 2k_2 w c^2 + 2k_{-2} b, \\ f_W &= 2k_1 a - k_2 w c^2 + k_{-2} b, f_T = \frac{1}{c_p} [k_1 a \Delta h_1 + (k_2 w c^2 - k_{-2} b) \Delta h_2] \end{aligned} \quad (1B)$$

(cf., e.g., [5]). Here, the symbols a , b , c , w denote the particle number density (mol cm^{-3}) of A, B, C, W and T is the temperature, Δh_1 , Δh_2 are the molar reaction enthalpies of the two reaction steps, and c_p is the heat capacity per unit volume. For the rate coefficients the Arrhenius equation

$$k_j = z_j e^{-E_j/RT}, \quad j = 1, \pm 2 \quad (2)$$

will be used. Together with an equation of state, e.g. $W = W(a, b, c, T)$, or with an equivalent other assumption (cf. eqn. 4), system (1) is a closed system determining the six unknown functions a , b , c , w , T , v_L of ζ , t . Other concepts of the description of the processes represented by (1) have been discussed in [6]. One of the various interdependency relations of the rates (1A), or (1B) allows one to deduce

$$\partial_t(a + 2b + c) + \partial_\zeta[(a + 2b + c)v_L] = 0 \quad (3)$$

from the first three equations of system (1).

REDUCED EQUATIONS

In the following, the system (1) with (1A), or (1B), respectively, will be rigorously simplified. Among various other assumptions, separations of slow and fast variables will be applied. Such separations are reasonable, if some ratios of rate coefficients and transport coefficients are small. A mathematical basis of slow-fast approximations is given in the theory of singular perturbations of PDEs (cf. [7]).

First, we assume that the main processes of the decomposition of the crystal take place within a comparatively small and almost homogeneous region (ζ_1 , ζ_2). This region is supposed closely to succeed the phase boundary at $\zeta = 0$, and to have a velocity

$$v_L = v_L(\zeta, t) \approx v_L(t) \quad (4)$$

Reactions at the phase boundary $\zeta = 0$ are excluded. With (4), the integral

$$a + 2b + c = a_0 = c_f = \text{const} \quad (5)$$

of (3) follows. This integral fulfills the condition of homogeneous distribution $a(\zeta) = a_0 = 1.3475 \times 10^{-2} \text{ mol cm}^{-3}$ of pure substrate A at $t = t_0 = 0$. In (5), it has been observed that the final state of the decomposition is a constant profile $c(\zeta) = c_f$ of pure C. The value $a_0 = c_f$ is smaller than the particle number density $c_{\text{crys}} = 2.1743 \times 10^{-2} \text{ mol cm}^{-3}$ of monocrystals of C. This consequence of (1) and (4) might be related to the porosity of the structure of the component C which is formed on heating samples of A.

Secondly, we assume that the substitutions

$$-\partial_\zeta(D\partial_\zeta w) + v_L\partial_\zeta w = M(w - \mu w_e) \quad (6)$$

$$-c_p\lambda\partial_\zeta^2 T + c_p v_L\partial_\zeta T = K(T - T_e) \quad (7)$$

can be used. In this equation, w_e and T_e denote the density of water vapor and the temperature in the surroundings of the crystal; μ is the equilibrium particle distribution coefficient at the surface of the crystal, and M , or K are supposed to be constant mean transition coefficients of transport of water, or heat, respectively, between the reaction zone and the exterior of the crystal.

Thirdly, we assume that the approximations

$$\partial_{\zeta} b \approx 0 \quad (8)$$

$$\partial_t a \approx 0 \quad (9)$$

are valid in the main part of the reaction zone, and for a considerable length of the reaction time. Equation (8) is motivated by the reversibility of the second reaction step of the mechanisms (A) or (B), and by the mobility of W. The relation (9) is based on the supposition $\partial_t a \gg \partial_t b, \partial_t w, \partial_t T$. This means that fast first steps of the reactions (A) or (B) lead to stationary profiles $a(\zeta, t) \approx a(\zeta)$ in a relaxation time which is short if compared with the long range time scale of the slow variables.

From (1, 4–9), one obtains the system

$$\begin{aligned} \dot{b} &= f_B \\ \dot{w} - M(\mu w_e - w) &= f_W \\ c_p \dot{T} - K(T_e - T) &= c_p f_T \end{aligned} \quad (10)$$

of three simultaneous ordinary differential equations (ODEs) with $(\dot{\cdot}) \equiv \partial_t$. This system determines the dependence of time of the functions b, w, T with the kinetics (A) or (B), respectively.

According to (1) and (9), the function $a = a(\zeta, t)$ on the right hand side of (10) has to be taken as an integral of

$$v_L \partial_{\zeta} a = f_A = \begin{cases} -2a^2 z_1 \exp(-E_1/RT) & \text{(A)} \\ +az_1 \exp(-E_1/RT) & \text{(B)} \end{cases} \quad (11)$$

(cf. (1), (2) and (9)) in which the unknown $T = T(\zeta, t)$ is involved, and where $v_L = v_L(t)$ is an arbitrary function. The relation (11) is fulfilled most simply if the density of A through the reaction zone is almost vanishing, i.e., $a \approx 0$. This value will hold, if A decomposes rapidly near the reaction front. On the other hand, it might also be supposed that the temperature T depends only very weakly on ζ , so that

$$k_1(T)/v_L(t) = Z \approx \text{const.} \quad (12)$$

Then (11) leads to

$$a \approx \begin{cases} (Z_0 + 2Z\zeta)^{-1} & \text{(A)} \\ Z_0 \exp(-Z\zeta) & \text{(B)} \end{cases} \quad (13)$$

where $Z_0 = \text{const}$. The profiles (13) decrease from the phase boundary $\zeta = 0$ towards the exterior of the crystal, if $Z_0 > 0$.

At $D = \text{const}$, eqns. (6) and (7) have solutions of the form

$$w(\zeta, t) = \mu w_e + \Omega_1(t) e^{\lambda_1 \zeta} + \Omega_2(t) e^{\lambda_2 \zeta} \quad (14)$$

$$T(\zeta, t) = T_e + \Theta_1(t) e^{\kappa_1 \zeta} + \Theta_2(t) e^{\kappa_2 \zeta} \quad (15)$$

where

$$\lambda_{1/2} = v_L/2D \pm \sqrt{v_L^2/4D^2 - M/D} \quad (16)$$

$$\kappa_{1/2} = v_L/2\lambda \pm \sqrt{v_L^2/4\lambda^2 - K/\lambda c_p} \quad (17)$$

The functions v_L , Θ_1 , Θ_2 , Ω_1 , Ω_2 of t have to be determined according to the algebro-differential problem (2, 10, 12, 14, 15). The roots of (16) and (17) are real and positive if $v_L^2 > 4MD$, and if $v_L^2 > 4K\lambda/c_p$. This case admits monotonous profiles of w , T which increase along the positive ζ -axis. On the other hand, at $v_L^2 < 4MD$, or $v_L^2 < 4K\lambda/c_p$, the profiles of w , T are oscillations which have increasing amplitudes on the ζ -axis. The dependence of T on ζ is weak, and (12) will hold, e.g., if $K/\lambda c_p$ is small and $\Theta_1 = 0$.

After these reductions, the vital point of the description of oscillating time structures of the decomposition is in the eqns. (10). These ODEs can be solved at given parameter values and initial conditions by standard numerical methods. They can have self-oscillating solutions if proper parameter values are chosen. In order to prove that, the Hopf-bifurcation theorem may be applied (cf., e.g., [8,9]). This can alternatively be proved by investigating some physically instructive special cases.

DECOUPLED SUBSYSTEMS OF TWO SIMULTANEOUS ODEs

In order to find cases in which (10) decouples into a separate ODE and a subsystem of two simultaneous ODEs admitting autoperiodic solutions we list various assumptions and the subsystems of two ODEs which follow from them.

I. Kinetics (A) at $k_- c^2 w \approx 0$

$$\begin{aligned} \dot{b} &= k_1 a^2 - k_2 b \\ c_p \dot{T} - K(T_e - T) &= 2k_1 a^2 \Delta h_1 + k_2 b \Delta h_2 \end{aligned} \quad (18)$$

Since $k_i \sim \exp(-E_i/RT)$, $i = 1, 2$, and since at fixed ζ the functions $a(\zeta, t)$ may be taken as a constant (cf. 2, 9), the eqns. (18) have exactly the form of the equations of a tank-reactor (CSTR) model given by Sal'nikov [10] and Frank-Kamenetskij [11]. This model, the SFK-CSTR, admits the

existence of self-oscillations, in principle. An extensive numerical investigation of this topic has been presented in [12] but, with the above suppositions which forbid back reactions of water, the existence of limit cycles of (18) is excluded by the Bendixon negative criterion (e.g., [13]) because of $\Delta h_1 < 0$, $\Delta h_2 < 0$.

II. Kinetics (A) at $\partial_t w \approx 0$ (cf. (9); slow-fast separation $\partial_t a \gg \partial_t w \gg \partial_t b, \partial_t T$)

$$\begin{aligned} \dot{b} &= k_1 a^2 + k_{-2} (a_0 - a - 2b)^2 w - k_2 b \\ c_p \dot{T} - K(T_e - T) &= 2k_1 a^2 \Delta h_1 + [k_2 b - k_{-2} (a_0 - a - 2b)^2 w] \Delta h_2 \end{aligned} \quad (19)$$

This system determines the dependence on time of b , T . In (19), the densities a , w may be regarded approximately as time-independent constants varying with ζ . If $a \approx 0$, $b \ll a_0$ is assumed, the system (19) goes over into a form of the SFK model which allows limit cycles. An even more voluminous region with auto-oscillations than in the subcase $a \approx 0$, $b \ll a_0$ must be contained in the higher-dimensional parameter space of (19). The existence of limit cycles of (19) hints at the importance of the reversibility of the second step of the mechanism (A) for oscillations.

If some self-oscillating solutions b , T of (19) have been computed, the faster function w is determined by the algebraic relation

$$w = \frac{M\mu w_e + 3k_1(T)a^2 + k_2(T)b}{M + k_{-2}(T)(a_0 - a - 2b)^2} \quad (20)$$

where (13) has to be substituted.

III. Kinetics (A) at $k_2 b \approx 0$, $b \ll a_0$

$$\begin{aligned} \dot{w} - M(\mu w_e - w) &= 3k_1 a^2 - k_{-2} w (a_0 - a)^2 \\ c_p \dot{T} - K(T_e - T) &= 2k_1 a^2 \Delta h_1 - k_{-2} w (a_0 - a)^2 \Delta h_2 \end{aligned} \quad (21)$$

At $M = 0$, (21) goes over into a SFK-system having limit cycles in the wT -plane, if the parameters at fixed ζ (cf. (9, 13, 15)) are chosen appropriately. Consequently, the eqns. (21) with $M \neq 0$ will also have self-oscillating solutions w , T . The existence of limit cycles of (A) at $k_2 b \approx 0$ suggests that the back reaction of the consecutive step of this mechanism is particularly important in the formation of oscillating time structures.

IV. Kinetics (B) at $k_{-2} b \approx 0$, $b \ll a_0$

If the exchanged meaning of the symbols k_{-2} , k_2 , Δh_2 of the mechanisms (A), (B) is taken into account, these assumptions agree with those of

the case (III). So do the equations which follow by them, if slight changes of the time-independent factors at $k_1(T)$ are disregarded.

V. Kinetics (B) at $\partial_t w \approx 0$ (cf. (9); slow-fast separation $\partial_t a \gg \partial_t w \gg \partial_t b, \partial_t T$)

One obtains equations and conclusions which essentially agree with those of the above case (II). Slight changes of the case (B) in comparison with (A) concern only the terms of the first reaction steps, and the exchanged meaning of the symbols k_{-2} , k_2 , Δh_2 .

VI. Kinetics (A), or (B) at $T = \text{const}$

The approximations (13) of (11) become exact results. From (10), two simultaneous ODEs with algebraic nonlinearities of third order in the variables b , w remain (k_1 , k_2 , $k_{-2} = \text{const}$). In order to prove the existence of limit cycles of these systems, theorems like that of Levinson-Smith (cf. ref. 14, p. 180) did fail. From this, we infer that probably no oscillations of the above reaction mechanisms will occur which are of chemical (isothermal kinetic) type.

CONCLUSIONS

The above discussion outlines physical aspects of a mathematical more advanced approximation of the proposed system of PDEs which has to be done. Notwithstanding the different restricting suppositions which lead from the PDEs (1) to the simultaneous systems of ODEs (10), the investigation makes evident that a rich class of thermokinetically oscillating consecutive decomposition reactions of solids could exist. The oscillating decomposition of gypsum at constant heating [1] might be subordinated to such self-oscillations. In this case, the exothermic heat effect of the back reaction of water into hemihydrate is an essential precondition of the oscillations. Isothermal chemical oscillations are rather unlikely.

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