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RECENT DEVELOPMENTS IN THE THEORY OF EMANATION THERMAL ANALYSIS

J. KŘÍŽ

Paint Research Institute, Sokolovská 16, 18600 Prague (Czechoslovakia)

V. BALEK

Nuclear Research Institute, 25068 Řež (Czechoslovakia)

ABSTRACT

A report of recent developments in the theory of the emanation thermal analysis of porous and dispersed solids is given. A mathematical model of the inert gas release during non-isothermal heating of solids is suggested, describing the behaviour of porous and dispersed solids on heating, taking into account the annealing of structure defects, recrystallization, sintering and the chemical reaction between particles of the powdered sample. Using the suggested model, it was possible to characterize the disorder state of solids and its changes, diffusion phenomena in solids, the kinetics of surface and structure changes and the reaction of zinc ferrite formation from zinc oxide and iron(III) oxide.

INTRODUCTION

Since Flügge and Ziemens [1] formulated their theoretical concept of the release of radioactive inert gases from solids, labelled by their radioactive parents, emanation thermal analysis (ETA) has been widely used for the study of various solid-state processes. However, these wide and theoretical studies by later workers [2–6] did not fulfil the requirements of the experimenters when dispersed or porous solids were studied by emanation thermal analysis.

The expressions derived by Flügge and Ziemens [1] are valid for isolated grains of solids, assuming a homogeneous and time-independent distribution of the inert gas in the sample. However, in emanation thermal analysis, the solids are commonly labelled by impregnation [7] of their surfaces with solutions containing radioactive parents of inert gases and a homogeneous distribution of the inert gas cannot be assumed. Also, a time-independent distribution of the inert gas in the sample cannot be assumed during the overall course of experiments during heating.

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The relationship between the radon release rate due to the recoil effect of radon atoms and the surface area of finely dispersed samples has been discussed by Quet et al. [9]; Beckman [6] derived a relationship between the radon release rate due to the recoil and diffusion from solids of various shapes, assuming different concentration profiles under both stationary and non-stationary conditions.

However, until recently a gap existed in the theory of the radon release rate from porous or finely dispersed solids during non-isothermal heating, taking into account the existence of various processes that may take place in the solids during heating. The aim of this paper is to outline the developments in the theory of ETA applicable to the evaluation of solid-state processes in porous and dispersed solids.

Theoretical consideration of the diffusion part of radon release. In porous solids, there appears to be a marked difference in the mobility of the emanating gas in the pores and in the solid matrix, at least at moderate temperatures. Therefore, we propose [1,2] to consider the emanation rate, ϵ_d, which is due to diffusion, as a sum of two different parts:

$$\epsilon_\mathrm{d} = \epsilon_\mathrm{dp} + \epsilon_\mathrm{ds} \tag{1}$$

Assuming a spherical shape of the solid under study (i.e., the smallest grain or, in a more abstract way of thinking, the elementary domain) and a cylindrical symmetry of the pore, the diffusion through the pore must follow the equation

$$\frac{\partial c(r,x,t)}{\partial t} = D_\mathrm{p}(t)\left[\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial x^2}\right]c(r,x,t) - \lambda c(r,x,t) + \zeta(r,t) \tag{2}$$

where c is the concentration of the gas, r is the radial and x the axial coordinate, respectively, λ is the decay constant and ζ is the source function. If the pore reaches the surface, the part ϵ_dp is then

$$\epsilon_\mathrm{dp} = \pi \int f(r_\mathrm{p}) r_\mathrm{p}^2 D_\mathrm{p}(T) \left.\frac{\partial c}{\partial x}\right|_{x=0} \mathrm{d}r_\mathrm{p} \tag{3}$$

where $f(r_p)$ is the distribution function of the pore radii, r_p. The solution of eqn. (2) can be found [2,3], knowing the functions $D_\mathrm{p}(t)$ and $\zeta(r,t)$. For $D_\mathrm{p}(T)$, we propose a combination of the Knudsen relationship and the usual Arrhenius-type function, viz.,

$$D_\mathrm{p}(T) = \alpha r_\mathrm{p}\left[\mathrm{e}^{-\beta}\sqrt{\frac{8R}{\pi M}}\,T^{1/2} + (1 - e^{-\beta}) d_\mathrm{p} \exp(-E_\mathrm{p}/RT)\right] \tag{4}$$

where α is a coefficient allowing a correction for the corrugation of the pore, and

$$\beta = b(1 - r_\mathrm{p}/\bar{l}_\mathrm{f}) \tag{5}$$

$\bar{l}_f$ being the mean free range of the gas atoms in the pore medium; as for the pore radius, we have to allow for the sintering process at elevated temperature, which has to follow some kinetics near to the form

$$-\frac{\mathrm{d}r_p}{\mathrm{d}T} = \frac{K_{ps}}{\kappa} r_p^a \exp(-E_{ps}/RT) \tag{6}$$

where the exponent a has been given a value of 1.

Considering now the source function $\zeta(T)$, we have to inspect three main cases: (a) simple diffusion through the solid matrix into the pore; (ii) direct emission of the atoms by recoil into the hollow of the pore; (iii) emission of the atoms into the opposite pore wall followed by escape of the atom via its own trajectory into the pore. We have shown [10–12] the forms of the respective source functions for these three mechanisms and we have demonstrated that (i) is operative at elevated temperatures only, (ii) may be important in the case of the macropores and (iii) seems to be the main mechanism and is fairly sensitive to the defectivity of the material. With the explicit forms of these functions, the solution of eqn. (2) can be found [11,12] by the Fourier method. A good agreement of the resulting model with numerous experimental results has been found [12,13].

For the pure diffusion of the gas in the solid, i.e., ϵ_{ds}, we assumed originally a perfect solid matrix, i.e., the diffusion equation

$$\frac{\partial c}{\partial t} = D_s\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]c - \lambda c + \zeta_s(r, t) \tag{7}$$

where r is now the radial coordinate of the spherical domain and the source function ζ_s is given by the decay of the parent isotope. With defective materials, however, different sites with individual mobilities of the gas atoms can be operative, e.g., interstitials, point defects, clusters or linear defects. Such a situation can be met approximately by a multi-channel model [14] in which parallel diffusion is considered in a number of channels, which are assumed to interact by the exchange of the diffusant. Defining k_{ij} as the probability of the transfer from the ith into the jth channel, the diffusion is described by the equation set

$$\frac{\partial c_i}{\partial t} = D_i\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]c_i - \left(\lambda + \sum_{j \neq i} k_{ij}\right)c_i + \sum_{j \neq i} k_{ji} C_j + \epsilon_i \zeta(T) \tag{8}$$

where ϵ_i is the volume fraction of the ith channel. The solution of this equation set for a two-site medium was given at this conference [5] and it is shown that even in this simplest case the interplay of the channels can give rise to some anomalies in the ETA curve.

This model can, however, be useful in a more general way. If the ith channel is, for instance, identified with the ith phase of the solid and if the fraction ε_i is dependent on temperature and time or, more exactly, is the function

$$\varepsilon_i = f(\varepsilon_1, \varepsilon_2, \ldots \varepsilon_n, T, t) \tag{9}$$

the set (8) can be used [15] as a model of a phase transition. More specifically, the diffusion under the conditions of a simple phase transition can be described by the equations

$$\frac{\partial c_1}{\partial t} = D_1\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]c_1 - (\lambda + k_{12}S)c_1 + k_{21}Sc_2 + \varepsilon_1\zeta(T) \tag{10a}$$

$$\frac{\partial c_2}{\partial t} = D_2\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]c_2 - (\lambda + k_{21}S)c_2 + k_{12}Sc_1 + \varepsilon_2\zeta(T) \tag{10b}$$

where S denotes the phase interface. Equations (10a) and (10b) describe the solid as a system of two mutually overlapping quasi-continua which are topologically interconnected by the interface S. In a more exact description, the original phase would be considered as a quasi-continuum, but the second as a statistical set of subdomains. The mathematical equivalent of such a description would be

$$\begin{aligned}\frac{\partial c_1(r,t)}{\partial t} &= D_1\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]c_1(r,t) - \lambda c_1(r,t)\\ &\quad - \frac{k_{12}D_{12}}{r^2}\int_0^{R_b - r}\pi(\rho)\rho^2 \left.\frac{\partial c_2(\rho, t)}{\partial \rho'}\right|_{\rho'=\rho} \mathrm{d}\rho\\ &\quad + \frac{k_{21}D_{21}}{r^2}\int_0^{R_b - r}\pi(\rho)\rho^2 \left.\frac{\partial c_1(r, t)}{\partial \rho'}\right|_{\rho'=\rho} \mathrm{d}\rho + \epsilon_1\zeta(T)\end{aligned} \tag{11a}$$

$$\begin{aligned}\left(\frac{\partial c_2(\rho', t)}{\partial t}\right)_{\rho, r} &= D_2\left[\frac{\partial^2}{\partial \rho'^2} + \frac{2}{\rho'}\frac{\partial}{\partial \rho'}\right]c_2(\rho', t) - \lambda c_2(\rho', t)\\ &\quad - \frac{k_{21}D_{21}}{r^2}\pi(\rho)\rho^2\frac{\partial c_1(r, t)}{\partial \rho'}\\ &\quad + \frac{k_{12}D_{12}}{r^2}\pi(\rho)\rho^2\frac{\partial c_2(\rho, t)}{\partial \rho'} + \tfrac{4}{3}\pi\rho^3\pi(\rho)\zeta(T)\end{aligned} \tag{11b}$$

where $\pi(\rho)$ is the differential probability that the subdomain of the second phase will have a radius in the interval $\langle \rho, \rho + \mathrm{d}\rho \rangle$, and will be coincident with the sphere of the radius r. (11b) is, in fact, an infinite set of equations. It can be shown [15] that these two descriptions, represented by the sets (10) and (11), are virtually equivalent.

There is, however, one additional possibility. The interphase boundary, or rather some area in the vicinity of it, could represent a state of high disorder and could thus serve as a separate diffusion channel with an exceptional mobility of the diffusant. This case is not included in our models and is under study now.

Up to this point, a homogeneous spherical domain of the sample has been considered. Although this can be a sufficient approximation in some instances, a more general description of the morphology should be available. For this purpose, we propose [15] the quasi-continuum-domain (QCD) model, which represents a hierarchy of spherical domains, each of which is considered as a diffusional continuum in which a statistical set of spherical subdomains is randomly distributed (the tightly packed set of interconnected subdomains being the limiting case). If N_n is the number of the subdomains of $(n-1)$th level in the domain of the nth level, the diffusion on the nth level is described by the approximate equation

$$\frac{\partial c_n(r,t)}{\partial t} = D_n\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]c_n(r,t) - \lambda c_n(r,t) + \sum_{i=1}^{N_n} \gamma_i(r)\epsilon_{n-1,i}(t) \quad (12)$$

where $\epsilon_{n-1,i}(t)$ is the flux of the emanating gas from the ith domain of the $(n-1)$th level, which consists of the surface recoil part, corrected for the trapping of the atoms by other subdomains, and of the diffusional part specific for the subdomain; $\gamma_i(r)$ is a factor expressing the probability of finding the boundary of the subdomain at the radius r. Expression (12) represents an equation set that can be simplified by two additional assumptions: (i) on the ith level, we consider uniform domains only; (ii) the diffusion on the $(i+1)$th level is much easier than on the ith level so that, for the ith level, it can be considered to be independent of the $(i+1)$th level. The second approximation is crude but it simplifies greatly the technical side of the solution. Under these approximations and after transformation, we obtain

$$\kappa\frac{\partial c_n(r,T)}{\partial T} = D_n(T)\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]c_n(r,T) - \lambda c_n(r,T) + \gamma_n'\epsilon_{n-1}(T) \quad (13)$$

where $\gamma_n \doteq 3N_n/4\pi R_n^3$. For $D_n(T)$, we consider the Knudsen diffusion and the sintering of the domain in all cases except $n=1$. The set (13) then has to be solved recursively, bearing in mind that ϵ_n must contain the recoil term, which, according to our approximation, is (for $n \geqslant 2$)

$$\epsilon_{r,n} \approx \psi(r_{b,n}/r_{b,1})^2\epsilon_{r,1} \quad (14)$$

where the factor ψ depends on geometrical relations.

No interphase chemical reaction has been considered so far. The ETA technique has also been found, however, to be a powerful tool for the study of such reactions. Therefore, our latest endeavour has been to establish a feasible theory of the ETA of topochemical reactions. We assume a spherical grain of a species A with a homogeneous distribution of the parent nuclide, which is in the contact with n_{AB} grains of the reaction partner B. In a combination of the models of Jander [16] and Komatsu [17], we assume [18] that the product is formed in small contact domains at first but, owing to fast surface diffusion, is spread quickly over the whole surface of the grain; for its thickness h, we propose the equation

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{\alpha D_{\mathrm{C}}^{(\mathrm{B})} \sigma n_{\mathrm{AB}}}{h} \tag{15}$$

where $D_{\mathrm{C}}^{(\mathrm{B})}$ is the diffusion coefficient of B in the product C, α is a constant and σ is the contact surface, which can be shown to be [19]

$$\psi = \pi \left[\beta D_{\mathrm{B}}^{(\mathrm{B})} R_b^2 (t - t_0)/kT \right]^{2/5} \tag{16}$$

where β is a constant.

Now, for the mathematical description of the gas diffusion from the reacting grain, the simplest way seems to be to express its diffusion coefficient by a continuous function (alternatively, we would have to solve a set of partial differential equations); we propose to do it by the approximation

$$D_{\mathrm{ef}}(r, T) = \omega D_{\mathrm{C}}(T) + (1 - \omega) D_{\mathrm{A}}(T) \tag{17}$$

where D_{C} and D_{A} are the diffusion coefficients of the gas in the product C or reactant A, respectively, and

$$\psi = \frac{1}{\pi} \operatorname{arccotg} \left[a \left(1 - \frac{r}{R_b - h} \right) \right] \tag{17a}$$

where h is the solution of eqn. 15; ω ensures a steep, although continuous, change of D_{ef} on the boundary between A and C. The diffusion is now described by the equation

$$\frac{\partial c}{\partial t} = \nabla \left[D_{\mathrm{ef}}(r, T) \nabla c \right] - \lambda c + \zeta(T) \tag{18}$$

which, in our approximation, can be transformed to

$$\kappa \frac{\partial c}{\partial T} = D_{\mathrm{ef}} \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \left(2 + \frac{\theta}{r} \right) \frac{\partial c}{\partial r} + \left(\frac{2\theta}{r} - \lambda \right) c + \zeta(T) \tag{19}$$

where

$$\theta = \frac{2}{r} D_{\mathrm{A}}(T) + \left(\frac{2\omega}{r} + \phi \right) \left[D_{\mathrm{C}}(T) - D_{\mathrm{A}}(T) \right] \tag{19a}$$

and

$$\phi = \frac{1}{\pi} \frac{(R_b - h)^2}{(R_b - h)^2 + a^2 (R_b - h - r)^2} \tag{19b}$$

For the diffusion coefficients, we generally assume an Arrhenius dependence on temperature. For product C, however, we have to allow for the structural change (e.g., crystallization) of its state which probably is, immediately after reaction, highly disordered. Assuming first-order kinetics of such a restructuring, i.e., for the fraction ε of the product in its original state,

$$-\frac{\mathrm{d}\varepsilon}{\mathrm{d}T} = \frac{K_{\mathrm{Cs}}}{\kappa}\varepsilon \exp(-E_{\mathrm{Cs}}|RT) \tag{20}$$

we obtain for D_{C}

$$\begin{aligned} D_{\mathrm{C}} &= D^{(1)}_{\mathrm{C},0} \exp\left[-E^{(1)}_{\mathrm{C}}/RT - \frac{K_{\mathrm{Cs}}}{\kappa}\int_{T_0}^{T}\exp(-E_{\mathrm{Cs}}/R\tau)\mathrm{d}\tau\right] \\ &\quad + D^{(2)}_{C,0}\left\{1 - \exp\left[-\frac{K_{\mathrm{Cs}}}{\kappa}\int_{T_0}^{T}\exp(-E_{\mathrm{Cs}}/R\tau)\mathrm{d}\tau\right]\right\}\exp(-E^{(2)}_{\mathrm{C}}/RT) \end{aligned} \tag{21}$$

where the superscripts (1) and (2) denote the original and the changed states, respectively. The emanation rate due to diffusion is then

$$\epsilon_{\mathrm{D}} = \kappa D_{\mathrm{C}} S \left.\frac{\partial c(r, T)}{\partial r}\right|_{r=R_b} \tag{22}$$

where S is the cross-section of the diffusion. The solution of eqn. (19), however, cannot be obtained in a closed form. We therefore solved it numerically and, by simulation, we have been able [18] to explain the existence of a typical peak on the ETA curve as a consequence of the reaction and restructuring process, both its form and its position being determined by the parameters of our model.

Finally, we should mention the use of the developed models, i.e., of the curve fitting problem. We have made a fairly extensive study of this problem, part of which was presented at this conference [14]. It seems that even with a powerful algorithm, such as the program CURFIT which has been developed by our research group, the above limit of the unknown parameters that can reasonably be found is about six.

We are currently attempting to find sensible approximations for routine work in the evaluation of the experimental data of emanation thermal analysis as published, e.g., in [20].

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