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EMANATION THERMAL ANALYSIS OF DEFECTIVE MEDIA THEORETICAL MODEL OF DIFFUSION IN A TWO SITE MEDIUM

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ABSTRACT

The diffusion part of the emanation power is analysed for a two site medium under quasi-stationary conditions. The emanation power is shown to depend on 6 independent parameters which may vary widely. The temperature dependence of the emanation power displays effects which could simulate structural changes of the material. The fitting of the parameters to the experimental curve,if more than 2 parameters are unknown and the experimental data are scattered too widely, needs a sofisticated optimization procedure.

INTRODUCTION

In the recently suggested model of the emanation thermal analysis (ETA) of defective materials[1,2], the homogeneity of the solid was supposed for the diffusion part of the emanation rate. Such ideal case is, however, met rarely by real materials. Therefore, the case of the diffusion in a medium with two sites of different mobility of the inert gas is discussed in this paper. Computer simulations of the model are presented as well as the complementary study of the curve fitting under various conditions.

THEORY

We consider here a solid sphere of the radius r_o with the homogeneous distribution of the parent nuclide c_o,which decays to the measured inert gas (the respective decay constants being λ_o and λ). If multiple sites of different mobility of the inert gas (e.g. interstitial positions and defects of various types) are present in the solid, the diffusion medium can be considered[3,4] as a multiple channel case. Usually, the statistical probability of the

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diffusant's transition from the i-th to the j-th channel can be characterized by some constant k_{ij}. The diffusion equation for the i-th channel is then

$$\frac{\partial c_i}{\partial t} = D_i\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]c_i - \left(\lambda + \sum_{j\neq i} k_{ij}\right)c_i + \sum_{j\neq i} k_{ji}c_j + \varepsilon_i\lambda_0 c_0 \qquad (1)$$

where c_i is the concentration of the diffusant in the i-th channel, D_i the diffusion coefficient and ε_i the volume fraction of the i-th channel, respectively. The equation set (1) can be transformed into one equation, namely

$$\frac{\partial \sum c_i}{\partial t} = \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]\sum D_i c_i - \lambda \sum c_i + \lambda_0 c_0 \,. \qquad (2)$$

Under rapid exchange, the steady state for each channel can be reasonably supposed, namely

$$c_i \sum_{j\neq i} k_{ij} = \sum_{k\neq i} k_{ki} c_k \qquad (3)$$

In such case, all variables but one can be eliminated from Eq.(2) by the usual methods of linear algebra. In the simplest case of two channels (e.g. interstitial positions of the perfect matrix and one type of defects), we obtain

$$\frac{\partial c_1}{\partial t}(1+K) = (D_1 + KD_2)\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]c_1 - \lambda(1+K)c_1 + \lambda_0 c_0, \qquad (4)$$

where $K = k_{21}/k_{12}$. Defining

$$D_{ef} = \frac{D_1 + KD_2}{1+K}, \qquad (5)$$

Eq.(4) gives the familiar form:

$$\frac{\partial c_1}{\partial t} = D_{ef}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]c_1 - \lambda c_1 + \frac{\lambda_0}{1+K}c_0 \,. \qquad (6)$$

Equations of this type can be solved rigorously (cf.[2,4]).For simplicity,however, we consider here the quasi-stationary conditions,i.e. $\partial c_1/\partial t \doteq 0$, which can be met by ETA in the case of a very slow heating. In this case, the already known[5] solution can be used and the diffusion part of the emanation power $\mathcal{E}_D$ is then

$$\mathcal{E}_D \doteq \frac{3}{y}\left(\coth y - \frac{1}{y}\right) \quad \text{, where} \quad y = r_0\sqrt{\lambda/D_{ef}} \qquad (7)$$

The usual Arrhenius temperature dependences $D_i = D_{io}\exp(-E_{Di}/RT)$ and $K = K_o\exp(E_K/RT)$ can be supposed, so that $\mathcal{E}_D$ has 6 independent parameters,namely $D_{1o}, E_{D1}, D_{2o}, E_{D2}, K_o$ and E_K.

SIMULATIONS OF THE MODEL

Examples of the computer simulations of the model are given in Figs. 1 to 4. The values of the parameters were: Fig.1: $D_{1o}=10^{-3}$, $E_{D1}=4x10^{4}$, $D_{2o}=0.5$, $E_{D2}=1.6x10^{4}$, $K_{o}=10^{-6}$, $E_{K}=3to8x10^{4}$; Fig.2: same as Fig.1, but $K_{o}=10^{-7}$ to 0.1, $E_{K}=6x10^{4}$; Fig.3: same as Fig.1, but $E_{D2}=1to3x10^{4}$, $E_{K}=6x10^{4}$ Fig.4: same as Fig.3, but $D_{2o}=10^{-4}$ to 1, $E_{D2}=1.5x10^{4}$.

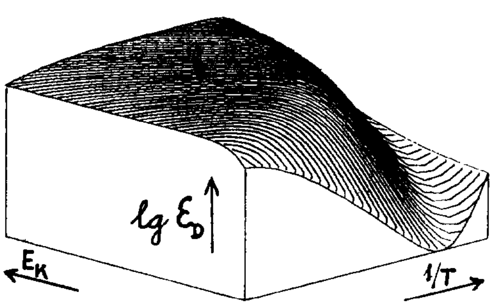

Fig.1: The E_K-1/T dependence of lg ε_D

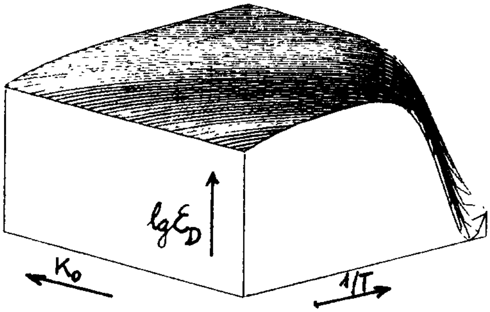

Fig.2: The K_o-1/T dependence of lg ε_D

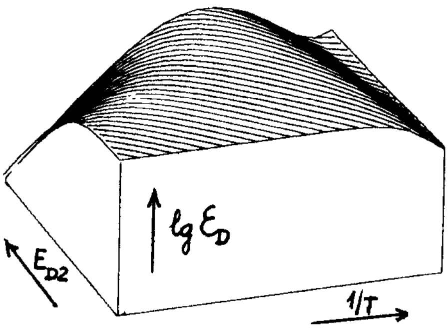

Fig.3: The E_{D2}-1/T dependence of lg ε_D

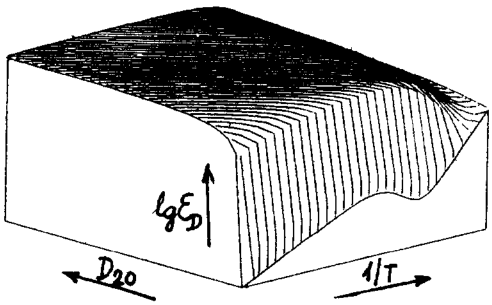

Fig.4: The D_{2o}-1/T dependence of lg ε_D

The interplay of the two different diffusion channels can, as should be clear from these examples, give rise to some peculiarities of the temperature dependence of ε_D, which could simulate nonexistent structural changes of the material.

THE FITTING OF THE PARAMETERS

In connection with the peculiarities of the temperature dependence of $\mathcal{E}_D$, the question of the fitting of the parameters′ values to the experimental curve is of importance. In our study, the "experimental" points were calculated exactly from the model and then scattered artificially by adding or substracting a random error in the given boundaries. In the same way, the experimenter′s "guesses" of the free (i.e. not fixed) parameters were randomly generated. As the basic fitting procedure, the FUnctional MInimization procedure by the LInear approximation (FUMILI)[6] was used. In some cases, the random direct search procedure was executed before FUMILI; this generally improved the convergence of the fitting iterations and did, in some cases at least, preclude the divergence or the trapping in a false optimum.

The fitting did not show any problems for the number of the optimized parameters up to 4, if the bounds of the parameters did not exceed +/- 50 percent in the case of E-s or x/: 10 in the case of $D_{io}(K_o)$, and the simulated experimental error did not exceed +/- 3 rel.percent. In these cases, the FUMILI procedure was able to find the correct parameters with the precision of 2 rel.percent in 7 to 10 iterations. In the case of 4 and more optimized parameters, the effectivity of the fitting was found to depend strongly on the level of the input information, i.e. on the number of experimental points and, especially, on their scattering; 50 experimental points and the 2 rel.percent error was found to be feasible for 4 free parameters. Nevertheless, even in these cases, the direct search procedure was advisable before FUMILI. In the case of 6 parameters, uncertainties and false optima were quite frequent.

The further improvement of the fitting procedure for this as well as for the previous[3] model is clearly needed and is under our investigation.

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