

## **THEORY OF EMANATION THERMAL ANALYSIS**

### **XI. Radon diffusion as the probe of microstructure changes in solids**

*I. N. Beckman<sup>1</sup> and V. Balek<sup>2</sup>*

<sup>1</sup>Department Chemistry, Moscow State University, 119899 Moscow, GSP-3, Russia

<sup>2</sup>Nuclear Research Institute Rez pic, CZ-250 68 Rez, Czech Republic

#### **Abstract**

The theoretical background for the use of radon diffusion as a probe of microstructure changes in solids is given. The high sensitivity of the emanation thermal analysis (ETA) in the study of solid state processes especially interactions taking place on surfaces and in the near surface layers is described. The increasing sensitivity of the method towards bulk processes with rising temperature is theoretically shown. The background considerations to be used in the mathematical modeling of temperature dependences of the radon release from solids on heating (i.e. simulated ETA curves) are presented. Various models for radon diffusion and various functions describing the annealing of structure irregularities, which served as diffusion paths for radon, were used in the modeling. It was shown, that ETA is able to characterize microstructure changes in the surface layers of the thickness from several nanometers to several micrometers.

**Keywords:** emanation thermal analysis, radon diffusion, structure defects annealing

#### **Introduction**

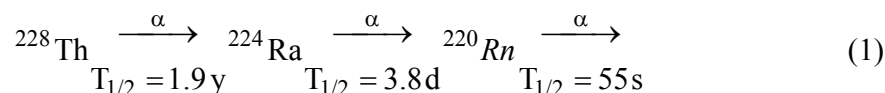
Emanation thermal analysis (ETA) has been widely used for the characterization of the evolution of surface area and opened porosity of the solids during heating [1-3]. The information obtained by ETA on the microstructure development of various solids was overviewed in a monograph by Balek and Tolgyessy [4]. The measured release of the inert gases, previously incorporated into the solids, made it possible to characterize the formation and annealing of structure defects. Various stages the inert gas mobility in the samples were described [6-18].

Different techniques were applied for the incorporation of the inert gas atoms (e.g. neon, argon, krypton, xenon and radon, resp.) into solid samples. Ion beam energy, energy of nuclear reactions, etc. were used for this purpose [5].

In this study we describe the theoretical approach for the evaluation of ETA results of the solids based on the release of radon atoms, which were incorporated into the near surface layers of the solids by the recoil energy of the spontaneous  $\alpha$ -decay of radon parents radionuclides.

#### **Background considerations**

Emanation thermal analysis [1] consists in the measurement of radon release rate from the samples previously labeled. Atoms of radon  $^{220}\text{Rn}$  are formed by the spontaneous  $\alpha$ -decay of  $^{228}\text{Th}$  and  $^{224}\text{Ra}$  according to the following scheme:



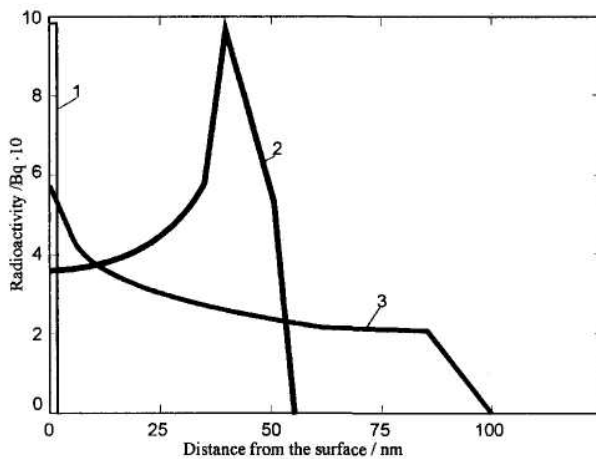
The thorium nuclide  $^{228}\text{Th}$  used for labeling samples has a suitable half-life (1.9 years) to serve as a

quasi-permanent source of radon  $^{220}\text{Rn}$  (half-life 55 s). The half-life of  $^{220}\text{Rn}$  ensures that the steady state between  $^{224}\text{Ra}$  and  $^{228}\text{Th}$  and  $^{224}\text{Ra}$  is established within several minutes, which makes it possible to investigate even rapid changes in the solids and on their surface. Radon formed by the spontaneous  $\alpha$ -decay of  $^{228}\text{Th}$  and  $^{224}\text{Ra}$  was incorporated into samples to a maximum depth of 100 nm from the surface, due to the energy ( $85 \text{ keV atom}^{-1}$ ) of recoiled atoms [5].

The method of sample labeling by  $^{222}\text{Rn}$  using the recoil energy of radium  $^{226}\text{Ra}$   $\alpha$ -decay was proposed by Lindner and Matzke [19]. Due to the half-life of  $^{222}\text{Rn}$  (3.8 days) the radionuclide of  $^{226}\text{Rn}$  cannot be used as the quasi-permanent source of radon atoms, in contrary to the radionuclides  $^{228}\text{Th} \rightarrow ^{224}\text{Ra} \rightarrow ^{220}\text{Rn}$ .

In the samples labeled by  $^{228}\text{Th}$  adsorption, the high amount of  $^{220}\text{Rn}$  is situated in the near surface layers. This ensures the high sensitivity of ETA to the changes of surface roughness and microstructure in the near surface layers. As it follows from the calculated concentration profiles (Fig. 1) the concentration of  $^{220}\text{Rn}$  has a descendent character. The Monte Carlo method was used in the calculation of the distribution profiles of  $^{224}\text{Ra}$  and  $^{220}\text{Rn}$  for a model sample. It was supposed that the parent  $^{228}\text{Th}$  radionuclide is situated on the surface of the sample up to the depth of several nanometers, corresponding to its roughness (Fig. 1, curve 1). The concentration profiles of  $^{224}\text{Ra}$  and  $^{220}\text{Rn}$  are given as curves 2 and 3, resp. in Fig. 1. During the calculation by Monte Carlo method and using TRIM code [20] we considered the solid sample of the density  $\rho=2.643 \text{ g cm}^{-3}$  (corresponding to yttria ceramics,  $\text{Y}_2\text{O}_3$ ). The calculated values of the recoil ranges are: for  $^{224}\text{Ra}$ : 47 nm (stragglng 15 nm), for  $^{220}\text{Rn}$ : 48 nm (stragglng 15 nm). It was supposed that the recoil energy of both  $^{224}\text{Ra}$  and  $^{220}\text{Rn}$  is  $85 \text{ keV atom}^{-1}$ , resp.

Moreover, it was supposed that  $^{228}\text{Th}$  and  $^{224}\text{Ra}$  do not migrate in the solid at the temperatures used for ETA measurements. The value of the total emanating rate  $E_{\text{TOTAL}}$  of a solid is composed of two terms, namely the emanating rate,  $E_{\text{R}}$ , due to recoil, and the emanating rate,  $E_{\text{D}}$ , due to diffusion. The emanating rate  $E_{\text{R}}$  depends on the shape and size of the sample, the recoil range of  $^{224}\text{Ra}$  and  $^{220}\text{Rn}$  in the sample and on the initial distribution of  $^{228}\text{Th}$ .



**Fig. 1** Calculated distribution profiles of the radionuclides  $^{228}\text{Th}$  (1) used for labeling of the sample by adsorption on the surface and radionuclides of  $^{224}\text{Ra}$  (2) and  $^{220}\text{Rn}$  (3) produced by  $\alpha$ -decay and introduced by the recoil energy into the dense solid plate

The emanating rate,  $E_{\text{D}}$  depends on the initial distribution function of  $^{220}\text{Rn}$ , surface area, the value of radon diffusion coefficient and its temperature dependence, and on the heating rate.

The total emanating rate  $E_{\text{TOTAL}}$ , representing the probability of the release rate of radon atoms from a solid, can be expressed in the simplified way as

$$E_{\text{TOTAL}}(T) = E_{\text{R}} + E_{\text{D}}(T) \quad (2)$$

where  $E_{\text{R}}$  is the emanating rate due to recoil (which is, for simplicity, taken as a constant value in this study), and  $E_{\text{D}}$  is the emanating rate due to diffusion. Two cases are considered in this paper: (A) no solid state

transitions take place during heating, (B) solid state transitions take place during heating.

(A) At the absence of the solid state transitions we suppose that the flux of radon from the sample (composed of grains smaller than 1 micron) is dependent on the sample size.

For powders of sub-micron grain size the radon flux is depending moreover on the sample shape. The following expression was proposed for the temperature dependence of  $E_D$  in the case of spherical grains [21]:

$$E_D = \frac{3}{y} \left[ \coth(y) - \frac{1}{y} \right]; \quad y = r_0 \left[ \frac{\lambda}{D(T)} \right]^{1/2} \quad (3)$$

$r_0$  is grain radius,  $\lambda$  is the decay constant of radon  $^{220}\text{Rn}$ ,  $D$  is radon diffusion coefficient in the solid,  $L_D = (D/\lambda)^{1/2}$  is called the diffusion length,  $\coth(y)$  representing the cotangent hyperbolic function of  $y$ .

The following temperature dependence was supposed for  $D(T)$ :

$$D(T) = D_0 \exp(-Q_D/RT) \quad (4)$$

where  $Q_D$  and  $D_0$  - are the activation energy and pre-exponential factor of radon diffusion, resp.,  $R$  - molar gas constant,  $T$  - temperature, K.

For the low values of  $E_D$  or for the large grain sizes the following simplified expressions can be used:

$$E_D = \frac{3}{y}; \quad y = r_0 \left[ \frac{\lambda}{D(T)} \right]^{1/2} \quad (4a)$$

$$E_D = \frac{3}{r_0 \left[ \frac{\lambda}{D(T)} \right]^{1/2}} = \frac{3}{r_0 (\lambda)^{1/2}} [D(T)]^{1/2} = \frac{3}{r_0} \left[ \frac{D_0}{\lambda} \right]^{1/2} \exp \left[ -\frac{Q_D}{2RT} \right] \quad (4b)$$

$$E_D = E_{D_0} \exp \left[ \frac{Q_D}{2RT} \right] \quad (4c)$$

The Eq. (4c) reflects the radon diffusion in an infinite media. It is applicable to samples of any shape (if the grain size is large enough, and coefficient of radon diffusion low enough). The temperature dependence of the radon flux from a homogeneous medium is usually described by a simple exponential curve.

If no chemical and physical changes take place in the homogeneous solid, under quasi-stationary conditions, the total emanating rate  $E_{\text{TOTAL}}$  depends on the temperature:

$$E_{\text{TOTAL}}(T) = \left( \frac{3x}{4} + \frac{x^3}{16} \right) + \frac{3}{y(T)} \left\{ \coth[y(T)] - \frac{1}{y(T)} \right\} \quad (5)$$

where  $x = R/r_0$ ,  $R$  is the path of the recoiled atoms of radon. Similar expressions were proposed [22, 23] for the grains of other shapes, such as plate or cylinder.

(B) In cases when the grains size, the concentration of defects and the radon diffusion coefficient in the solid samples change, additional effects on the temperature dependence on the radon release rate appear. Consequently, the changes in defects concentration can be revealed by the measurement of the radon release directly on heating in the required gas. Different mechanisms of radon diffusion in the disordered heterogeneous solid were considered in the proposed model, namely:

- diffusion in two (or more) independent paths (parallel diffusion);
- diffusion permitting the reversible exchange of the radon atoms between paths (dissociative diffusion);

- diffusion in a solid where the creation of new diffusion paths and/or the annealing of the existing paths is supposed (dissociative diffusion in dynamic regimes);
- diffusion in a solid where solid state transitions take place during heating (reactive diffusion);
- the consecutive inert gas diffusion.

## Models of radon diffusion in solids

### Model of parallel diffusion

According to this model both the radon release due to the diffusion in pores ( $E_{D_i}$ ) and that due to the diffusion in bulk of the sample ( $E_D$ ) contribute to the emanating rate  $E_D$  value. Considering the model for parallel diffusion the emanating rate  $E_D$  can be written as follows:

$$E_D(T) = \varphi_1 E_{D_1}(T) + \varphi_2 E_{D_2}(T) \quad (6)$$

where

$$\begin{aligned} \varphi_1 + \varphi_2 &= 1; \\ E_{D_1} &= \frac{3}{y_1} \left[ \coth(y)_1 - \frac{1}{y_1} \right]; \quad E_{D_2} = \frac{3}{y_2} \left[ \coth(y)_2 - \frac{1}{y_2} \right]; \\ y_1 &= r_0 \left( \frac{\lambda}{D_1(T)} \right)^{1/2}; \quad y_2 = r_0 \left( \frac{\lambda}{D_2(T)} \right)^{1/2}; \\ D_1 &= D_{1,0} \exp\left(-\frac{Q_1}{RT}\right); \quad D_2 = D_{2,0} \exp\left(-\frac{Q_2}{RT}\right) \end{aligned}$$

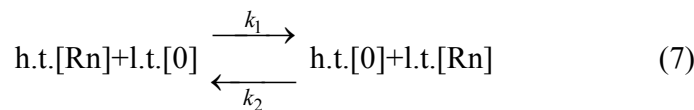
where  $\varphi_i$  is concentration of diffusion path of  $i$ -types,  $D_{0,i}$  is the pre-exponential factor and  $Q_i$  is activation energy of radon diffusion along the paths of  $i$ -type.

### Model of dissociative diffusion

In the mathematical model of inert gas diffusion it is assumed that at least two channels of radon diffusion control the diffusion. The radon concentration can be described as distributed between two types of traps in the lattice, differing in the thermal stability. The respective traps of the inert gas are called in this paper as ‘high temperature traps’ and ‘low temperature traps’. It has been supposed that clusters can be formed between the traps and inert gas atoms. ‘High temperature clusters of radon’ are denoted h.t. [Rn] and ‘low temperature clusters of radon’ are denoted l.t.[Rn]. The h.t.[Rn] cluster is more temperature stable than the l.t.[Rn] cluster, therefore the former predominated at higher temperatures, whereas the latter cluster predominated at low temperature interval of the sample heating.

When the temperature increases, the mobility of the low temperature clusters increases and the emanating rate,  $E$ , of the solid increases correspondingly. The dissociation of these clusters also increases, as the result of trapping of radon in the low-mobile stage (i.e. as the h.t.[Rn] high temperature clusters increases).

The reversible process of the formation of high mobile radon clusters (i.e. the l.t.[Rn] clusters) can be described by Eq. (7):



where h.t.[Rn] is radon situated in a high temperature, (low-mobile) cluster, l.t.[0] is an unoccupied low temperature defect; h.t.[0] is an unoccupied high temperature defect; l.t.[Rn] is radon in a low-mobile

cluster;  $k_1$  is the rate constant for l.t.[Rn] cluster formation;  $k_2$  is rate constant for l.t.[Rn] cluster decomposition.

For the conditions of a thermal equilibrium we introduced the equilibrium constant  $K$  of the reversible redistribution of radon between low temperature and high temperature defects, respectively. We assumed that the defects are in the thermal equilibrium, i.e. that  $N_1 + N_2 = N$ , where  $N_1$  is the concentration of high temperature defects;  $N_2$  is the concentration of low temperature defects; and  $N$  is the total defect concentration. The constant  $K$  characterizing the formation of the l.t.[Rn] complex is expressed by Eq. (8):

$$K = \frac{C_2 N_1(0)}{C_1 N_2(0)} = \frac{C_2(N_1 - C_1)}{C_1(N_2 - C_2)} = \frac{k_1}{k_2} \quad (8)$$

where  $C_1$  and  $C_2$  are the radon concentrations in high temperature and low temperature defects, respectively; and  $N_1(0)$  and  $N_2(0)$  are the concentrations of the respective unoccupied defects.

It is to point out that the tracer concentration of radon is used for the labeling of solids to be investigated by means of the emanation thermal analysis, so that  $C_1 \ll N_1$  and  $C_2 \ll N_2$ . Then

$$\frac{C_2}{C_1} = \frac{k_1 N_2}{k_2 N_1} = K \frac{\varphi_2}{\varphi_1} = K^* \quad (9)$$

where  $\varphi_1 = N_1/N$  and  $\varphi_2 = N_2/N$  are the relative concentration of high and low temperature defects, respectively ( $\varphi_1 + \varphi_2 = 1$ ).

The inert gas migration in two kinds of diffusion channels, where the inert gas atoms are exchanged, can be formally described by the kinetics of the first order chemical reaction.

The system of differential equations that describes such a process is given in Eq. (10).

$$\begin{aligned} \frac{\partial C_1}{\partial t} &= D_1 \frac{\partial^2 C_1}{\partial x^2} - k_1 \varphi_1 C_1 + k_2 \varphi_2 C_2 \\ \frac{\partial C_2}{\partial t} &= D_2 \frac{\partial^2 C_2}{\partial x^2} - k_1 \varphi_1 C_1 + k_2 \varphi_2 C_2 \end{aligned} \quad (10)$$

where  $D_1$  and  $D_2$  is the radon diffusion coefficient along the high temperature and the low temperature defects, respectively.

In the presence of a local equilibrium ( $k_1 \varphi_1 C_1 = k_2 \varphi_2 C_2$ ) the diffusion process is described by the effective diffusion coefficient  $D_{\text{eff}}$  given in Eq. (11):

$$D_{\text{eff}} = \frac{D_1(T) + K(T) \varphi_2 D_2(T)}{1 + K(T) \varphi_2} \quad (11)$$

The terms of Eq. (8) obey the following temperature dependencies

$$D_1 = D_{10} \exp\left(-\frac{Q_1}{RT}\right) \quad (12a)$$

$$D_2 = D_{20} \exp\left(-\frac{Q_2}{RT}\right) \quad (12b)$$

$$K = K_0 \exp\left(-\frac{Q_K}{RT}\right) \quad (12c)$$

where  $Q_1$  and  $Q_2$  are the activation energies of radon diffusion via the high and low temperature defects respectively;  $Q_K$  is the enthalpy of l.t.[Rn] complex formation;  $D_{10}$ ,  $D_{20}$ , and  $K_0$  are the respective pre-exponential factors; and  $R$  is the molar gas constant.

If the migration of radon from one diffusion channel into another can be described by the equilibrium constant,  $K(T)$  (Eq. (12c)) the *mechanism of the dissociative diffusion* should be used for the modeling and the evaluation of the ETA curves. In this case the emanating rate  $E_D$  depends on temperature as follows:

$$E_D = \left[ \frac{D_{20} \exp\left(-\frac{Q_2}{RT}\right) + D_{10} \exp\left(-\frac{Q_1}{RT}\right) \varphi_2(T) K_0 \exp\left(\frac{Q_K}{RT}\right)}{1 + K_0 \varphi_2 \exp\left(\frac{Q_K}{RT}\right)} \right]^{1/2} \quad (13)$$

In the modeling of more complex cases of the thermal behavior of solids, we have considered not only the values of the radon diffusion permeability in individual diffusion channels, but also the relative number,  $\varphi_2(T)$ , of the diffusion channels. Then, the following expression was used for the temperature dependence of  $E_D$ :

$$E_D = \left[ \frac{D_{20} \exp\left(-\frac{Q_2}{RT}\right) + D_{10} \exp\left(-\frac{Q_1}{RT}\right) \varphi_2 K_0 \exp\left(\frac{Q_K}{RT}\right)}{1 + K_0 \varphi_2(T) \exp\left(\frac{Q_K}{RT}\right)} \right]^{1/2} \quad (14)$$

A problem raised in the determination of the temperature dependence of the concentration of easily mobile, low temperature defects,  $\varphi_2(T)$ . To solve the problem we assumed that:

- $\varphi_2$  is independent on temperature in the case, if radon diffusion takes place via impurity defects, or if l.t.[Rn] clusters dissociation is faster than that of the most mobile low temperature defects;
- $\varphi_2(T)$  is a function that decreases during annealing of defects (e.g., radiation or mechanically induced defects);
- $\varphi_2(T)$  is a stepwise function that decreases over a narrow temperature intervals in which a phase transition takes place in the solid.

For these assumptions we can write:

$$\varphi_2(T) = \varphi_2^0 \left[ 1 - \left(\frac{A}{2}\right) \left\{ 1 + \operatorname{erf}\left(\frac{T - T_m}{\sigma\sqrt{2}}\right) \right\} \right] \quad (15)$$

or

$$\varphi_2(T) = \varphi_2^0 \left[ 1 - \left(\frac{A}{2}\right) \left\{ 1 + \operatorname{erf}(z) \right\} \right]$$

where  $\varphi_2^0$  is the initial concentration of low mobile defects,  $A$  is constant that determines the concentration range of the transition,  $0 < A < 1$ ;  $T_m$  is the temperature of maximum rate of defects concentration change;  $\sigma$  is a constant that determines the temperature range of transition  $\Delta T$  (where  $\Delta T = 3\sigma$ ),  $\operatorname{erf}(z)$  is integral Gauss function

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} e^{-\xi^2} d\xi; \quad z = \frac{T - T_m}{\sigma\sqrt{2}}$$

and  $\xi$  is a variable of integration.

### *Model of reactive diffusion*

If solid-state transitions take place in the investigated sample, the temperature dependence of the total emanating rate,  $E$ , can be schematically written as:

$$E(T) = E_R + E_D(T) \Psi(T) \quad (16)$$

i.e. the second term is a product of two functions:  $E_D$  characterizing the radon permeability of diffusion channels, and the  $\Psi(T)$  characterizing structural changes during solid state reactions.

In the case that the sample, undergoing solid state transitions is heated to elevated temperature, the temperature dependence of the radon diffusion coefficient  $D(T)$  is a growing function, whereas the  $\Psi(T)$  is the descending function.

The character of the ETA curve depends on a number of diffusion paths serving for the gas release,  $\Psi(T)$  function characterizing the microstructure changes in the solid and  $D(T)$  function characterizing permeability of transporting paths. The shape of the ETA curve is therefore determined as the combination of various functions  $\Psi(T)$  and  $D(T)$ . In this study we used several types of functions for  $D(T)$ , for example:

$$D(T) = D_0 \exp\left(-\frac{Q_D}{RT}\right) \quad (17a)$$

$$D(T) = D_{10} \exp\left(-\frac{Q_{10}}{RT}\right) + D_{20} \exp\left(-\frac{Q_{20}}{RT}\right) \quad (17b)$$

$$D = \frac{D_{20} \exp\left(-\frac{Q_2}{RT}\right) + D_{10} \exp\left(-\frac{Q_1}{RT}\right) K_0 \exp\left(-\frac{Q_K}{RT}\right)}{1 + K_0 \exp\left(-\frac{Q_K}{RT}\right)} \quad (17c)$$

$$D = \frac{D_{20} \exp\left(-\frac{Q_2}{RT}\right) + D_{10} \exp\left(-\frac{Q_1}{RT}\right) K_0 \varphi(T) \exp\left(-\frac{Q_K}{RT}\right)}{1 + K_0 \varphi(T) \exp\left(-\frac{Q_K}{RT}\right)} \quad (17d)$$

In the case that the number of diffusion paths and/or surface area decreases on heating, the structural function  $\Psi(T)$  has a decreasing character, whereas if the number of diffusion paths increases during the heating of the sample the structural function  $\Psi(T)$  has an increasing character.

In the modeling, following expressions were used for the structural function  $\Psi(T)$ . The descending character is described by the functions given in Eqs (18a)-(18e), whereas the increasing character of the defects concentration can be expressed by functions given by Eqs (18f) and (18g), resp.

$$\Psi(T) = \exp(-qT) \quad (18a)$$

$$\Psi(T) = T^m \quad (18b)$$

$$\Psi(T) = \frac{1}{1 + \left(\frac{T}{T_m}\right)^p} \quad (18c)$$

$$\Psi(T) = \frac{1}{1 + \exp\left(-\frac{T - T_m}{\Delta T}\right)^p} \quad (18d)$$

$$\Psi(T) = 1 - 0.5 \left[ 1 + \operatorname{erf} \left\{ \frac{1 - \frac{T_m}{T}}{\frac{\Delta T \sqrt{2}}{T}} \right\} \right] \quad (18e)$$

$$\Psi(T) = \exp(qT) \quad (18f)$$

$$\Psi(T) = 0.5 \left[ 1 + \operatorname{erf} \left\{ \frac{1 - \frac{T_m}{T}}{\frac{\Delta T \sqrt{2}}{T}} \right\} \right] \quad (18g)$$

where  $q$ ,  $m$ ,  $T_m$  and  $T$  are parameters.

The following general expression was proposed for the mathematical modeling of the overall view ETA curves:

$$E(T) = E_0 + \sum_{i=1}^n \rho_i D_{i0} \exp\left(-\frac{Q_i}{2RT}\right) + \sum_{j=1}^m \rho_j D_{j0} \exp\left(-\frac{Q_j}{2RT}\right) \Psi_j(T) \quad (19)$$

The functions  $D(T)$  and  $\Psi(T)$  are determined by the mechanisms of chemical or physical processes.

### *Mechanism of consecutive diffusion*

The mechanism of consecutive diffusion assumes, that in a temperatures range  $T_0 \leq T \leq T_1$  the radon diffusion takes place in the initial material (characterized by parameters  $D_{10}$  and  $Q_1$ ), and in the temperature range  $T_1 \leq T \leq T_2$  radon diffusion takes place in the newly formed structure (characterized by the parameters  $D_{20}$  and  $Q_2$ ).

In the more complex models of the consecutive diffusion we considered the possibility of the smooth transition from one structure to another via a series of intermediate states. Monotonous functions of the transition from  $D_{10}$  to  $D_{20}$  and from  $Q_1$  to  $Q_2$  were used in the modeling.

### **Simulation of temperature dependences of radon diffusion**

The following considerations should be taken in the modeling of the temperature dependences of radon diffusion (simulated ETA curves) which describe the thermal behavior of the solids.

The effects observed on the ETA curves can be ascribed to the following processes:

- thermal desorption of radon from the surface and near surface pores and cracks connected with the surface
- mobility of radon along grain boundaries and other structure defects serving as diffusion paths for radon
- changes in the concentration of the radon diffusion paths, which may increase in the early stage of the solid state transition due to the formation of the new paths, and decrease in the latter stage due to the structure ordering of the newly formed phase.

The observed peak-like effects on the ETA curves therefore reflect the initial increase of radon diffusion paths or surface area, followed by their decrease due to the annealing of the diffusion paths.

The expressions (18a-g) can be used in the modeling of both the decrease (Eqs (18a-e)) of the surface area and the concentration of the structure defects and their respective increase (Eqs (18f, g)).

The changes in the surface area or porous structure of solids are reflected by the emanating rate  $E_R$  and  $E_D$  in a different way.

Sintering of grains or collapse of porosity is reflected by the decrease of the radon release rate. The decrease of the surface area can be described by parabolic, exponential or other descending (symmetrical or asymmetrical) functions, respectively. For the multicomponent solids, the values of the radon diffusion parameters may differ in each component and depend on the surface area available for radon migration from the sample.

During the thermal decomposition of the sample intermediate metastable structures are formed, which may considerably differ in the number of radon diffusion paths, surface area and open porosity. The



metastable phases may possess different surface relief and roughness. The newly formed interfaces may exist only temporarily and disappear on further heating or cooling of the samples. The existence of such interfaces (even not observable by XRD and surface area measurement by nitrogen adsorption) can be revealed by means of ETA based on the measurement of radon release. The changes in the radon diffusion mechanisms may take place during thermal treatment of the sample.

The mathematical model, designed in this study, takes into account that the thickness of the analyzed layer by means of ETA increased during heating of the sample, due to the increasing value of the radon diffusion length  $L_D=(D/\lambda)^{1/2}$  at elevated temperatures. The values of the diffusion length  $L_D$  were calculated supposing the temperature dependence of  $D(T)$  given in Eq. (17a), where  $D_0=6 \text{ m}^2 \text{ s}^{-1}$ ,  $Q_D=209.5 \text{ kJ mol}^{-1}$ . As it follows from Table 1, the radon diffusion length calculated for a model ionic solid of the density of  $2.643 \text{ g cm}^{-3}$  considerably increased with heating. By this way the thickness of the layer which became labeled by radon increased from 1.6 nm at  $800^\circ\text{C}$  up to 6900 nm at  $1400^\circ\text{C}$ .

Table 1 Diffusion length for radon in a model solid characterized by the density  $\rho=2.643 \text{ g cm}^{-3}$ ,  $D_0=6 \text{ m}^2 \text{ s}^{-1}$ ,  $Q_D=209.5 \text{ kJ mol}^{-1}$

Temperature/ $^\circ\text{C}$	Diffusion length $L_D/\text{nm}$
20	$1.6 \cdot 10^{-29}$
800	1.6
900	11
1000	62
1100	261
1200	902
1400	6900

In practice it means that ETA is able to reflect the microstructure changes, not only in the near surface layers, labeled by recoil, but also in the bulk of the solid sample. In the low temperature range where the radon diffusion in the solid matrix is negligible, the mechanism of the thermo-stimulated desorption of radon atoms from the structure defects and traps can be considered in the evaluation of ETA results.

Examples of the mathematical simulation of the temperature dependences of the radon release rate will be presented in the next study [24], considering different solid state processes like thermal decomposition of hydroxides, defect concentration changes due to nonstoichiometry etc.

## Conclusions

It was shown in this paper that radon diffusion can serve as a probe of microstructure changes in solids. The thickness of the layer in which ETA is able to characterize microstructure changes increases from several nanometers to several micrometers with the sample heated from  $800$  up to  $1400^\circ\text{C}$ , respectively. The mathematical models described in this paper can be used for the modeling and evaluation of the ETA experimental results. The theoretical basis for ETA was upgraded giving mathematical models for the computer treatment of ETA data, and finally, making the application of ETA easier.

## References

- 1 V. Balek, J. Thermal Anal, 35 (1989) 405.
- 2 V. Balek, Thermochem. Acta, 192 (1991) 1.
- 3 V. Balek, E. Klosova, J. Malek, J. Šubrt, J. Bohacek, P. Bezdička, A. Watanabe and T. Mitsuhashi, Thermochem. Acta, 340-341 (1999) 301.
- 4 V. Balek and J. Tölgyessy, Emanation Thermal Analysis and Other Radiometric Methods, in

Wilson and Wilson (Eds), *Comprehensive Analytical Chemistry*, Vol. XIIC, Elsevier, Amsterdam 1984, p. 302.

- 5 F. W. Felix, *J. Physique*, 34 (1973) C9-149.
- 6 S. Kalbitzer, *Z. Naturforsch.*, 17A (1962) 1071.
- 7 P. Koss, *Acta Physica Austriaca*, 26 (1967) 251.
- 8 E. V. Kornelsen, *Can. J. Phys.*, 42 (1964) 364.
- 9 Č. Jech and R. Kelly, *J. Phys. Chem. Sol.*, 30 (1969) 465.
- 10 H. J. Matzke, *J. Nucl. Mat.*, 21 (1967) 190.
- 11 R. Kelly, *Can. J. Chem.*, 38 (1961) 663.
- 12 R. Kelly and H. J. Matzke, *J. Nucl. Mat.*, 17 (1965) 179.
- 13 H. J. Matzke, *Nucl. Appl*, 2 (1966) 131.
- 14 S. Ong and T. S. Elleman, *J. Nucl. Mat.*, 42 (1972) 191.
- 15 P. Schmeling, *J. Phys. Chem. Sol.*, 28 (1967) 1185.
- 16 Č. Jech, *Nature*, 178 (1956) 1343.
- 17 G. Carter and J. S. Colligon, *Ion bombardment of solids*, Heinemann, London 1968.
- 18 H. J. Matzke, *Rad. Effects*, 3 (1970) 93.
- 19 R. Lindner and H. J. Matzke, *Z. Naturforsch.*, 15A (1960) 1082.
- 20 J. F. Ziegler and J. P. Biersack, *The stopping and range of ions in solids*, Pergamon Press, New York 1985.
- 21 K. E. Zimens, *Z. Phys. Chem., Part A*, 192 (1943) 1.
- 22 K. B. Zaborenko and O. A. Kapustin, *Radiokhimia*, 16 (1974) 611.
- 23 T. N. Gregory and S. Moorbatch, *Trans. Far. Soc.*, 47 (1951) 844.
- 24 V. Balek, V. Zeleňák, I. N. Beckman, J. Rouquerol, P. Llewellyn and J. Subrt, *J. Therm. Anal. Cal.*, to be published.