THEORY OF EMANATION THERMAL ANALYSIS XII.
Modelling of radon diffusion release from disordered solids on heating

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The background for the modelling of radon diffusion release from disordered solids is given and used for the simulation of emanation thermal analysis results characterizing the annealing of structural irregularities that serve as radon diffusion paths in the solids.

Introduction

Emanation thermal analysis (ETA), based on the measurements of the radon release from samples previously labelled, makes it possible to characterize microstructural changes that accompany phase transitions and/or chemical transformations in solids or on their surfaces [1, 2]. The changes of surface and subsurface structural irregularities, which serve as paths for radon diffusion, can be monitored under *in situ* conditions of the sample treatment [3]. The ETA has been applied to solve various problems of material chemistry, *e.g.* to determine optimized conditions for preparation of catalysts, sorbents, waveguides and other advanced materials, to characterize the thermal stability of porous and nanostructural materials [4–13]. Information about microstructure changes that took place during in situ heating of layered natural and synthetic clay minerals was obtained by ETA [14–16]. Papers published in recent years [17, 18] are a source of the theory of modern ETA.

In this paper results of the modelling of radon release due to diffusion from solids (as influenced by the annealing of structural irregularities) are presented.

Background for the modelling of ETA results

Emanation thermal analysis is based on the release of radon from samples previously labelled with traces of [228]Th and [224]Ra as parent isotopes of [220]Rn. [228]Th (half-life 1.9 years) is a quasi-permanent source of [220]Rn (half-life 55 seconds). Processes in solids can then be characterized by the measurement of the radon released from the samples under 'in-situ' conditions of heat treatment [2–4].

Several mechanisms of radon release from the labelled samples have been proposed: (*i*) release due to the recoil energy of the radon atoms, (*ii*) diffusion in open pores, inter-granular space or interface boundaries and (*iii*) bulk diffusion of radon in the matrix of the solid.

It has been demonstrated in numerous papers, e.g. [3–16], that processes like annealing of surface roughness, changes of surface area, collapse of porous structures of solids or interlaminar space of layered clay minerals can be characterized by ETA. The radon release due to diffusion, (E_D), and the radon release due to recoil, (E_R), reflect such changes in different ways.

The total value of the emanation rate measured during the ETA experiments can be expressed as:

$$E(\text{total}) = E_R + E_D(T) \qquad (1)$$

For inorganic ionic solids E_R, the emanation rate due to recoil, can be considered as the value of emanation rate at room temperature because the value of the emanation rate due to diffusion, $E_D(T)$, can be neglected at room temperature.

Values of both the E_R and $E_D(T)$ depend [4] on the size and shape of the sample (grain size and surface roughness) and the migration (mobility) of radon atoms by diffusion $E_D(T)$, is determined by the average diffusion path $(D/\lambda)^{1/2}$ of radon [220]Rn atoms.

The radon release from solids when no structural or chemical transformations take place on heating was already described in [4]. Taking into account this traditional approach [4] the temperature dependence of the emanation rate $E_D(T)$ from a solid can be expressed by Eq.(2) :

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$$E_D(T) = \frac{3}{r_0}\left(\frac{D(T)}{\lambda}\right)^{1/2} \cdot$$

$$\cdot \left\{ \mathrm{Coth}\left[r_0\left(\frac{\lambda}{D/T}\right)^{1/2} - \frac{1}{r_0}\left(\frac{D(T)}{\lambda}\right)^{1/2}\right]\right\} \quad (2)$$

where $D(T)$ is the radon diffusion coefficient, $\lambda=0.12$ s^{-1} is the decay constant of the radionuclide ^{220}Rn, $(D/\lambda)^{1/2}$ is the average radon diffusion length, and r_0 is the size of grains. The temperature dependence of the radon diffusion coefficient $D(T)$, was assumed to be:

$$D(T)=D_0\exp(-Q_D/RT) \quad (3)$$

where D_0 is pre-exponential factor which depend on the number of diffusion paths and their availability for radon atom migration, Q_D is the activation energy of radon migration (its value is composed from value of the activation energy of the escape of radon atoms from the traps in the solid sample and the activation energy of the migration along diffusion paths in the solid), R is the molar gas constant, and T is temperature in K.

When no changes in size, shape or structure of the solid take place on heating, the temperature dependence of the radon diffusion coefficient of a homogeneous solid sample, can be described by the simple exponential dependence given in Eq. (3). When physical transitions or chemical transformations take place on heating the solid, the temperature dependence of the total emanation rate $E(T)$ can be expressed by Eq. (4):

$$E(T)=E_R+E_D(T)\Psi(T) \quad (4)$$

where second term is a product of two functions: $E_D(T)$, characterizing the radon permeability along structural irregularities in the solid which serve as diffusion paths, and $\Psi(T)$, characterizing the changes in the number of the radon diffusion paths caused by microstructural changes in the solid. The $D(T)$ function in Eq. (3) can be used for characterization of the radon permeability of the transporting paths, so the shape of the ETA curve in Eq. (4) is therefore determined by the product of the functions $\Psi(T)$ and $D(T)$.

The temperature dependence of the rate constant k for solid-state transitions is assumed to be of the Arrhenius type:

$$k=k_0\cdot\exp(-\Delta E_a/RT) \quad (5)$$

where E_a is the activation energy of the solid-state process, k_0 is the pre-exponential factor, R is the molar gas constant and T is the temperature in K.

The selection of a $\Psi(T)$ function suitable for the modelling is not an easy task. Its character is determined by the mechanism and kinetics of the solid state reaction. Moreover, new phases can be formed primarily on surface, grain boundaries or in the volume of sample. A number of mathematical expressions was proposed [19–21] for the description of these processes. If the mechanism of the solid-state reaction is known e.g. from the DTA, TG or EGA measurements, so equations formally proposed for the respective reaction kinetics can be used in the modeling of the ETA results. In such case the $\Psi(T)$ function, that describe the changes in the number of radon diffusion paths during the solid state process, is derived from the respective kinetic function obtained by other thermal analysis methods. In this study we shall present two cases as examples how to express the $\Psi(T)$ function by using the respective expressions of the non-isothermal reaction kinetics .

1. If a first order reaction is assumed:

$$\psi(T) = e^{-g(T)} \quad (6a)$$

where $g(T) = \dfrac{k_0 E_a}{R\beta}10^{-2.315-0.4567\frac{E_a}{RT}}$ β is the linear heating rate: $T=T_0+\beta t$,
where T_0 is the onset temperature of sample heating.

2. If a sintering mechanism is assumed

$$\psi(T) = \exp\left[-k_0\exp\left(-\frac{E_a}{RT}\frac{T-T_0}{\beta}\right)\right] \quad (6b)$$

β is the linear heating rate: $T=T_0+\beta t$,
where T_0 is the onset temperature of sample heating.

In the determination of the $\Psi(T)$ function for the modeling of ETA results of more complex topochemical processes mathematical descriptions should be used that were presented e.g. in monographs [22, 23].

In cases when the mechanism of the solid state transformations is not known the $\Psi(T)$ function can be assessed by using the integral Gauss approach:

$$\Psi(T) = 1 - \frac{A}{2}\left[1 + erf\left(\left(1-\frac{T_m}{T}\right)\left(\frac{\Delta T\sqrt{2}}{T}\right)^{-1}\right)\right] \quad (6c)$$

where T_m is the temperature at which the maximum rate of annealing of the structural defect that serves as the radon diffusion path occurs, ΔT is the temperature interval of the respective solid- state process and A is a parameter describing the contribution of the respective solid-state process to the change in the number of the radon diffusion paths, $0<A<1$.

If total annealing is achieved on heating the sample, we assume that $\Psi(T)\to0$, $A=0.5$, erf is the integral Gauss function

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

where σ is a constant that determines the temperature range of transition ΔT (where $\Delta T = 3\sigma$) and ξ is a variable of integration [18].

When the rate of the diffusion paths annealing can be determined, we suggest the use of Eq. (7) to calculate the temperature dependence of the $\varphi(T)$ function as the first derivative of the $\Psi(T)$ function.

$$\varphi(T) = -\frac{d\Psi(T)}{dT} \qquad (7)$$

For the determination of E_a and k_0 for the annealing process we suggest the use of thermal analysis measurements under several different heating rates, β, and the calculation the of the E_a from the dependence of the temperature the of peak maximum, T_m, on β (Eq. 8), as used in the non-isothermal kinetics of solid state processes from the results of TG and DTA [24–26]. As for TG or DTA methods, the characteristic maximum, T_{max}, on the ETA curves has to correspond to a constant degree of transformation, α

$$\ln\left(\frac{\beta}{T_{max}}\right) = -\frac{E_a}{RT_{max}} \qquad (8)$$

From ETA results the permeability to radon of the structure of a disordered solid can be determined. This parameter is of practical importance because the size of a radon atom is comparable to the size of a water molecule. ETA also provides information about the temperature dependence of radon transport properties in the disordered solids and thermal annealing of the surface and subsurface structural irregularities which serve as radon diffusion paths.
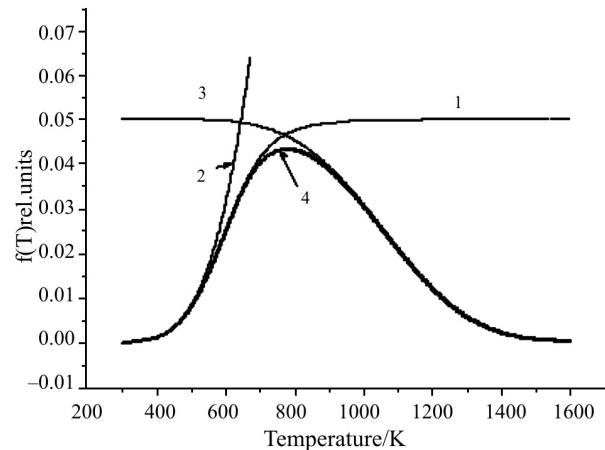
Results of the modelling of radon diffusion in disordered solids during heating

The aim of the modelling was to simulate the temperature dependence of the radon release rate and to characterize the effect of the annealing of structural irregularities, which serve as radon diffusion paths. The effect of the kinetic parameters of sintering on the temperature dependence of radon diffusion in disordered solids is demonstrated in Figs 1–3.

Figure 1 depicts the results of the modelling of processes considered to influence the radon mobility in the solid sample. Equation (2) was used for the modelling of curve 1. The temperature dependence of radon diffusion $E_D(T)$ is presented as curve 2, assuming that no annealing of surface disorder takes place in the sample in the temperature range considered. (Eq. (3) was used for the modelling of curve 2). Curve 3 depicts the temperature dependence of the $\Psi(T)$ function that describes the annealing of the structural irregularities. (Eq. (6b) was used for the modelling of

curve 3). Curve 4 depicts the temperature dependence of the model that corresponds to the product $E_D(T) \cdot \Psi(T)$ (Eq. (4) was used for the modelling of curve 4).

To determine the maximum rate of the modelled process in the solid, Eq. (7b) is used. Results of the modelling are presented in Fig. 2: curve 1 corresponds to the temperature dependence of radon release from the sample, curve 2 is the $\Psi(T)$ function that describes the annealing of the structure, curve 3 depicts the temperature dependence $d[E_D(T)]/dT$ as

Fig. 1 Results of mathematical modelling of radon diffusion from disordered solids, curve 1 – temperature dependence of $E_D(T)$ under absence of radon diffusion paths annealing (Eq. (2) was used in the modelling), curve 2 –temperature dependence of the of $D(T)$ (Eq. (3) used in the modelling), curve 3 – temperature dependence of $\Psi(T)$ (Eq. (6b) used in the modelling), curve 4 – temperature dependence of $E_D(T) \cdot \Psi(T)$ (Eq. (4) and Eq. (6b) were used in the modelling)
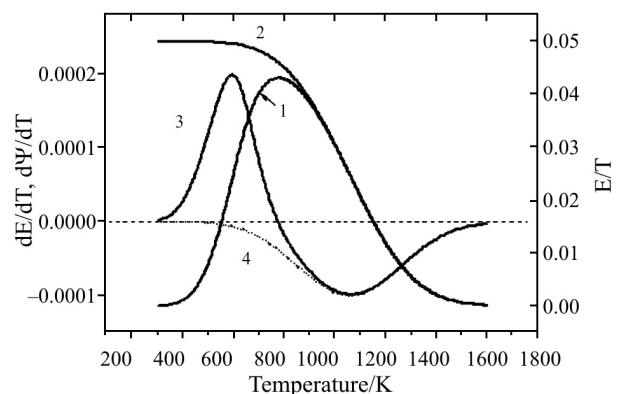
Fig. 2 Mathematical modelling of radon diffusion from disordered solids, curve 1 – temperature dependence of $E_D(T) \cdot \Psi(T)$. (Eq. (4) and Eq. (6b) were used in the modelling), curve 2 – temperature dependence of $\Psi(T)$. (Eq. (6b) used in the modelling), curve 3 – temperature dependence of $d[E_D(T) \cdot \Psi(T)]/dT$, curve 4 – temperature dependence of $\varphi(T) = d[\Psi(T)]/dT$ (Eq. (7) and Eq. (6b) were used in the modelling)
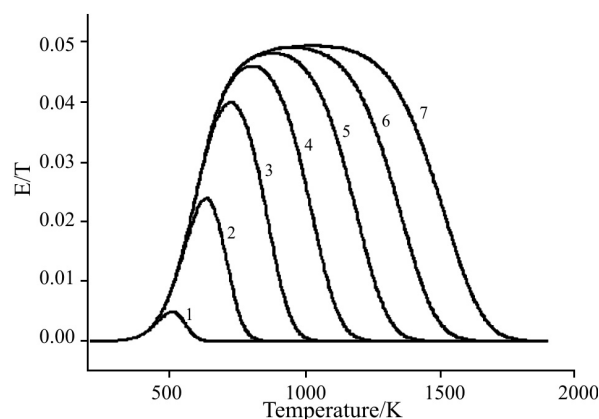
Fig. 3 Temperature dependences of $E_D(T)$. $\Psi(T)$ supposing following values of parameters for the annealing of radon diffusion paths: $E_a=5$ kJ mol^{-1}, $R=8.31$ J K^{-1} mol^{-1}, $Z=0.1$, $D_0=7000$ cm^2 s^{-1}, $Q_D/R=4000$ K, $T_0=280$ K, $A_0=1$, $\beta=5$ K^{-1} min^{-1}, the values of E_a/R varied from 5000 K (for curve 1) to 17000 K (for curve 7).

the first derivative of $E_D(T)$, curve 4 corresponds to the $\varphi(T)$ function as the first derivative of the function $\Psi(T)$ (calculated by using Eq. (7)). The singular points of the respective derivative curves were used for the determination of the temperatures of maximum rates of the modelled processes.

In Fig. 3 the temperature dependences of radon release rate are presented, assuming different kinetics parameters for the annealing process. The $\Psi(T)$ function in Eq. (6b) was used to model the decrease in the number of radon diffusion paths. Equation 2 was used for the temperature dependence of the radon release rate $E_D(T)$; it was assumed that $E_R \approx 0$.

The following parameters were used in the modelling: $E_a=5$ kJ mol^{-1}, $R=8.31$ J K^{-1}mol^{-1}, $Z=0.1$, $D_0=7000$ cm^2 s^{-1}, $Q_D/R=4000$ K, $T_0=280$ K, $A_0=1$, $\beta=5$ K^{-1} min^{-1}, the values of E_a/R varied from 5000 K (for curve 1) to 17000 K (for curve 7).

It follows from Fig. 3 that the character of the temperature dependence of $E_D(T)$ depends on the E_a value: for the higher E_a values the decrease of the radon release rate takes place at higher temperatures than for the lower E_a values.

Conclusions

By mathematical modelling it was demonstrated that emanation thermal analysis can be advantageously used in the characterization of the annealing of structural irregularities that serve as radon diffusion paths. Such data cannot be obtained by means of other thermal analysis techniques under in situ conditions of heating. By using mathematical models for the evaluation of the ETA experimental data it is possible to

determine the diffusion permeability of the disordered solids as well as the thermal stability of their disordered stage. The experimental verification of the results of ETA modelling has been carried out for samples of various advanced materials in the form of powders, thin films and porous slabs. The comparison of the experimental ETA results and the results of the mathematical modelling for these samples will be described in the next study in this journal.

Acknowledgements

References

1 V. Balek, J .Tölgyessy, Emanation Thermal Analysis and Other Radiometric Emanation Methods, In: Wilson and Wilson's Comprehensive Analytical Chemistry, Part XIIC,(Ed. by G. Svehla), Elsevier Science Publishers, Amsterdam, 1984, p. 304.

2 V. Balek and M. E. Brown, Less common techniques, in: Handbook on Thermal Analysis and Calorimetry, Vol. 1, Chapter 9. (Ed. by M. E. Brown), Elsevier Science B. V. 1998, pp. 445–471.

3 V. Balek, J. Subrt, T. Mitsuhashi, I. N. Beckman and K. Gyoryova, J. Therm. Anal. Cal., 67 (2002) 15.

4 V. Balek, Thermochim. Acta, 22 (1978) 1.

5 V. Balek, T. Mitsuhashi, J. Subrt, S. Bakardjieva and Z. Malek, J. Therm. Anal. Cal., 72 (2003) 119.

6 L. A. Perez- Maqueda, J. M. Criado, C. Real, V. Balek and J. Subrt, J. Eur. Cer. Soc., 22 (2002) 2277.

7 V. Balek, V. Zelenak, T. Mitsuhashi, I. N. Beckman, H. Haneda and P. Bezdicka, J. Therm. Anal. Cal., 67 (2002) 63.

8 V. Balek, V. Zelenak, T. Mitsuhashi, S. Bakardjieva, J. Subrt and H. Haneda, J. Therm. Anal. Cal., 67 (2002) 83.

9 J. Poyato, L. A. Perez-Maqueda, M. C. Jimenez de Haro, J. L. Perez-Rodriguez, J. Subrt and V. Balek, J. Therm. Anal. Cal., 67 (2002) 73.

10 V. Balek, T. Mitsuhashi, A. Watanabe, V. Zelenak, J. Subrt, P. Bezdicka and J. Bohacek, J. Colloid Interface Sci., 260 (2003) 70.

11 V. Balek and Z. Malek, J. Subrt. M. Guglielmi , P. Innozenzi, V. Rigato and G. Della Mea, J. Therm. Anal. Cal., 76 (2004) 43.

12 V. Balek, N. K. Labhsetwar, T. Mitsuhashi, H. Haneda, J. Subrt and V. Zelenak, J. Mater. Sci., 39 (2004) 13.

13 V. Balek, J. Subrt, J. Rouquerol, P. Llewellyn, V. Zelenak, I. M. Bountsewa, I. N. Beckman and K. Gyoryova, J. Therm. Anal. Cal., 71 (2003) 773.

14 L. A. Perez-Maqueda, V. Balek, J. Poyato, J. L. Perez-Rodriguez, J. Subrt, I. M. Bountsewa, I. N. Beckman and Z. Malek, J. Therm. Anal. Cal., 71 (2003) 715.

15 F. Kovanda, V. Balek, V. Dornicak, P. Martinec,
    M. Maslan, L. Bilkova, D. Kolousek and I. M. Bountsewa,
    J. Therm. Anal. Cal., 71 (2003) 723.
16 J. Poyato, L. A. Perez-Maqueda, A. Justo and V. Balek,
    Clays Clay Miner., 50 (2002) 791.
17 V. Balek and I. N. Beckman, J. Therm. Anal. Cal.,
    67 (2002) 37.
18 I. N. Beckman and V. Balek, J. Therm. Anal. Cal.,
    67 (2002) 49.
19 J. D. Tretyakov, Solid-state reactions, Publ. House
    'Khimia', Moscow, 1978 (in Russian), p. 98.
20 E. Koch, Non-isothermal reaction analysis, Plenum Press,
    New York, 1978, p.67.
21 J. H. Flynn, in: 'Thermal Analysis (2.ICTA)', Vol.2,
    Academic Press, New York 1969, p.1111.

22 J. Sestak, Termophysical properties of solids: Their mea-
    surements and theoretical thermal analysis, Academia
    Prague, 1984, pp. 172–259.
23 M. E. Brown, D. Dollimore and A. K. Galwey, Reactions
    in the solid state (in: Comprehensive chemical kinetics,
    Vol.2), Elsevier, Amsterdam 1980, pp. 103–201.
24 ASTM E 698, Standard test method for Arrhenius kinetics
    constants for thermally unstable materials.
25 J. P. Elder, J. Thermal. Anal., 30 (1985) 657.
26 J. Opferman and E. Kaisersberger, Thermochim. Acta,
    11 (1992) 167.