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THEORY OF EMANATION THERMAL ANALYSIS. II *. IMPROVEMENT AND COMPUTER SIMULATION OF THE MATHEMATICAL MODEL FOR INERT GAS RELEASE FROM A POROUS SOLID

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ABSTRACT

An improved mathematical model for the inert gas release from porous solids is proposed. The idea of the recoil atoms' escape via migration along their recoil path and via diffusion in a quasi-continuum, simulating the highly defective solid, has been introduced in this model. The improved model takes into account the mechanism of the inert gas diffusion in the solid matrix which is significant at temperatures above 0.3–0.5 times the absolute melting temperature of the respective solid. The expressions derived describe the behaviour of the inert gas release from porous solids during a non-isothermal treatment.

Computer simulations of the improved model justified the application of the model in the description of the thermal behaviour of porous solids.

The dependence of the ETA curves on porosity (i.e., the number of pores and their radii), diffusion coefficient, constants of the sintering kinetics, as well as on the heating rate are shown graphically.

A comparison of the theoretical and experimental ETA curves of silica gel, obtained under linear heating rate, is given.

INTRODUCTION

Emanation thermal analysis (ETA) is based [1,2] on the measurement of the release rate of a radioactive inert gas from a solid previously labelled by the same gas or by some of its radioactive parent nuclides. The release of inert gas atoms, born by the decay of an incorporated parent nuclide, from a porous solid, proceeds by several distinct mechanisms: (i) the recoil of the inert gas atoms from the surface layer of the parent nuclide; (ii) the injection

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* For Part I see ref. 3.

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of the inert gas by recoil into the hollow of the pores, followed by rapid diffusion; (iii) the migration of the recoil atoms, trapped by the pore wall either in a mobile position or in a defect, to the inner pore surface, followed by rapid diffusion through the pore; (iv) the inert gas diffusion in the solid matrix, contributing significantly at elevated temperatures, i.e., in most cases, at temperatures higher than one third of the solid's melting point. Each of the above mechanisms contributes to the total value of the emanation rate [1] of the porous solid.

The mathematical model of the inert gas release kinetics, suggested in Part I of this series [3], neglected, for the sake of simplicity, mechanism (iv) and also partly ignored process (iii). This resulted, however, in impairing the universal applicability of the model. Therefore, the original model was improved to take into account, in rather good approximation, mechanisms (i)–(iv).

Extensive simulations were made in the whole range of the sensible values of empirical constants, using the ICL 7-42 computer of the University Computer Center in Prague. Representative examples of these simulations are presented in this paper.

THEORY

The original form of the model

As shown previously [3], the emanation rate of a porous body $\epsilon(T)$ can be described by the equation

$$\epsilon(T) = \epsilon_R + \epsilon_P + \epsilon_S \tag{1}$$

where the increments on the right-hand side correspond to surface recoil, pore diffusion and the diffusion in the solid, respectively; from these, ϵ_S had been neglected

$$\epsilon_R = \frac{\pi}{2}\frac{\rho_r}{\rho_R} R_b \Lambda_T c_T \left(R_b + \tfrac{1}{3}\rho_r\right) \tag{2}$$

for the homogeneous distribution of the parent nuclide, and

$$\epsilon_P = \frac{N_p \pi^{3/2} r_{p0}^3}{l} \exp\left[-\frac{1}{\kappa}\left(\lambda \Delta T + 3K_p J_T\right)\right] \sum_{n=0}^{\infty} \left(n + \tfrac{1}{2}\right)\left[b_n(T) + c_n(T)\right] \tag{3}$$

Here, T is the absolute temperature, κ the linear heating rate, R_b the radius of the spherical body, N_p the number of its pores having the initial radius r_{p0} and the length l, c_T the concentration of the parent nuclide (e.g., ^{228}Th), λ and Λ_T the decay constants of the inert gas (^{220}Rn) and the parent nuclide, respectively, ρ_r and ρ_R the recoil range of the inert gas and the intermediate nuclide atoms (^{224}Ra), respectively. The meaning of the remaining symbols is as follows

$$b_n(T) = \frac{2}{l}\frac{\zeta(0)}{\lambda}\left\{\frac{1}{\beta_n} - \frac{1}{\alpha^2+\beta_n^2}\left[\beta_n - \frac{\alpha}{\sinh(\alpha l)}\right]\right\}\exp\left(-\frac{n^2\pi^2}{\kappa l^2}\tau_0\right) \tag{4}$$

$$c_n(T) = \frac{2}{\kappa l}\exp\left(-\frac{n^2\pi^2}{\kappa l^2}\right)\int_{T_0}^{T}\zeta(s)\exp\left[\lambda s + \frac{\pi^2 n^2}{\kappa l^2}\tau_s\right]\mathrm{d}s \tag{5}$$

where

$$\alpha = \left[\frac{\lambda}{r_{p0}}\sqrt{\frac{\pi M}{8RT_0}}\right]^{1/2} \tag{6a}$$

and

$$\beta_n = \left(n + \tfrac{1}{2}\right)\frac{\pi}{l} \tag{6b}$$

The integrals are

$$\tau_x = r_{p0}\sqrt{\frac{8R}{\pi M}}\int_x^T \phi^{1/2}\exp\left[-\frac{K_p}{\kappa}J_\phi\right]\mathrm{d}\phi \qquad (x = T_0,\ s) \tag{7}$$

and

$$J_\phi = \int_{T_0}^{\phi}\exp(-E_p/R\chi)\mathrm{d}\chi \tag{8}$$

The inert gas creation function $\zeta(T)$ for the pore diffusion, which appears in eqns. (4) and (5), had the original form

$$\zeta(T) = \Lambda_T c_T \gamma\left[\left(1-\frac{\gamma}{2}\right) - \left\{1 - \frac{\gamma}{2} - \frac{4r_p}{\rho'_r}\left[1 - \frac{r_p\gamma}{\rho'_r}\ln(1-\gamma)\right]\right\} \times\left[1 - p_0\exp(-E_e/RT)\right]\right] \tag{9}$$

where $\gamma = \rho_R/\rho_r$, ρ'_r denotes the recoil range of the inert gas atoms in the pore medium (e.g., air), and p_0, E_e are phenomenological coefficients of the migration rate of the recoil atoms trapped by the pore's wall; K_p and E_p are the constants of the pore sintering kinetics.

The expression (9) reflects the assumption that, at a sufficiently high temperature, almost all recoil atoms which had been trapped by the pore wall are released immediately into the pore. This rather crude simplification leads, according to our computer simulations, to an exponential form of the very first part of the theoretical ETA curve, which gives a bad fit with the experiments. Therefore, the first improvement of the original model has been done by a closer inspection of this problem.

The modification of the creation function ζ(T)

The usual inner medium of the pores is air or some other gas in which the range of the recoiled atoms is at least two orders of magnitude longer than their range in the solid. The recoil atoms thus hit the opposite wall at various angles and with various energies from 0 to 85 keV, depending on the depth from which they are emitted. In agreement with the ion bombardment studies (cf. e.g., refs. 4,5), we can, in first approximation, suppose all such recoil atoms to be primarily trapped by the wall. Their backward migration into the pore, which should be reflected by the function $\zeta(T)$, can probably proceed by three different processes (cf. ref. 6): (i) the rapid backward migration of the atom along its own trajectory; (ii) the relatively rapid diffusion of the atoms along the systematic (e.g., linear) defects already present in the material; (iii) the moderately rapid diffusion of the atoms on the high-mobility sites (e.g., interstitial positions) of the solid matrix; in addition to this we should consider (iv) the slow diffusion process of atoms trapped in point defects or other low-mobility sites. The last of these, however, can be excluded immediately on our level of approximation and in the case of the short-living radioactive atoms and the relatively easy sintering of the pores. To avoid unmanageable complications, we propose to neglect process (iii) as well in the following mathematical treatment. In other words, the atom can escape in the new version of the model either along its own original trajectory or along the already present systematic defect if it meets one. Both alternatives have the common feature that the escape proceeds via a linear defect and that such an escape path can, by a minor rearrangement of the surrrounding solid, become a trap (point or cluster defects being the sites of much lower mobility than, e.g., interstitial positions [6]). There is, however, a serious difference here, that in the first case the escape path is destroyed rapidly by the relaxation of the solid matrix whereas, in the second one, the dissipation is brought about by a much slower thermal rearrangement.

Escape of an atom via its own trajectory

Let $\pi(\theta, \mathrm{x}, t_0)$ be the differential probability that in the interval $\langle t_0, t_0 + \mathrm{d}t \rangle$ an atom will be emitted from the depth $\langle x, x + \mathrm{d}x \rangle$ in the direction $\langle \theta, \theta + \mathrm{d}\theta \rangle$, its trajectory length in the opposite wall being $l_{\theta,x} = \rho_\mathrm{r} - x \cos \theta$, if the passage through the pore is neglected. Under homogeneous distribution of the parent nuclide, the probability is [3]

$$\pi(\theta, x, t_0) = \frac{\rho_\mathrm{r} - x}{2\rho_\mathrm{r}} \Lambda_\mathrm{T} c_\mathrm{T} \tag{10}$$

The backward migration of the atom must proceed by thermally activated random jumps in one dimension of the trajectory. In spite of the fact that we are dealing with a single particle here in contrast to the statistical ensemble considered in classical diffusion, virtually the same relations must hold for the probabilistic density function (quantum effects being neglected) of the particle as they do for the concentration in the usual case. We can thus write for the probabilistic density $\pi(\xi, t)$ on the point $\xi \epsilon \langle l_{\theta,x}, 0\rangle$ and the instant t:

$$\frac{\partial \pi(\xi, t)}{\partial t} = D_e(T)\frac{\partial^2 \pi(\xi, t)}{\partial \xi^2} - \lambda \pi(\xi, t) \tag{11}$$

with the initial condition

$$\pi(\xi, t_0) = \pi(\theta, x, t_0)\delta(x - l_{\theta,x}) \tag{12}$$

where $\delta(x - l_{\theta,x})$ is the Dirac delta function. $D_e(T)$ in eqn. (11) is a function analogous to the diffusion coefficient. The familiar Arrhenius form of such a function suggested by the thermal activation of the migration jumps must, however, be complicated by the change of the energy barrier due to the restoration of the solid matrix. We propose to treat this problem in the following way. In a mild simplification, the migration path can be pictured as a statistical mixture of a population ϕ of the low energy barrier E_e and of the population $(1 - \phi)$ of the high energy barrier E_e'. For the change of ϕ, first-order kinetics can be reasonably supposed

$$-\frac{d\phi}{dT} = \frac{p_r}{\kappa}\exp(-E_r/RT)\phi \tag{13}$$

If we neglect the penetration through the high energy barrier E_e', the function $D_e(T)$ thus takes the form

$$D_e(T, T_0) = p_e \exp\left[-E_e/RT - \frac{p_r}{\kappa}\int_{T_0}^{T}\exp(-E_r/R\sigma)d\sigma\right] \tag{14}$$

where T_0 is the temperature corresponding to the time of the recoil event. Transforming eqn. (11) into the temperature-dependent form and introducing the variable

$$\tau_{e,T_0} = \frac{1}{\kappa}\int_{T_0}^{T} D_e(\sigma, T_0)d\sigma \tag{14a}$$

we obtain the solution in the form of a Green's function,

$$\pi(\xi, T) = \frac{\pi(\theta, x, T_0)}{2(\pi\tau_{e,T_0})^{1/2}}\exp\left[-\frac{(\xi - l_{\theta,x})^2}{4\tau_{e,T_0}} - \frac{\lambda}{\kappa}(T - T_0)\right] \tag{15}$$

From this, the part of the creation function due this type of escape is

$$\begin{aligned}\zeta_e(T) &= \int_{T_0}^{T}\int_{\rho_r}^{0}\int_{0}^{\arccos(x/\rho_r)} D_e(T, \sigma)\left.\frac{\partial \pi(\xi, \sigma)}{\partial \xi}\right|_{\xi=0} d\theta dx d\sigma \\ &= \frac{\Lambda_T c_T}{\pi}\int_{T_0}^{T} D_e(T, \sigma)\tau_{e,\sigma}^{-3/2}\left\{\frac{\rho_r}{4} - \frac{\tau_{e,\sigma}}{\rho_r}\left[1 - \exp\left(-\frac{\rho_r^2}{4\tau_{e,\sigma}}\right)\right]\right\} \\ &\quad \times \exp\left[-\frac{\lambda}{\kappa}(T - \sigma)\right]d\sigma\end{aligned} \tag{16}$$

where $\tau_{e,\sigma}$ is analogous to expression (14a) with the integration from σ to T. The integral in eqn. (16) cannot be expressed in a closed form; for numerical integration, the interval from $T - 4\kappa t_{0.5}$ to T ($t_{0.5}$ being the half-time of the gas) has been found to be quite appropriate to give sufficient precision.

Escape of an atom via diffusion

In accordance with the previous considerations, there is some probability that, in a highly defective material, the recoil atom can finally enter some continuous defect which will allow its rapid migration to the pore wall; such a probability is given by a factor ϵ, which is proportional or equal to the volume fraction of such defects in the vicinity of the pore. As such defects can be of different length and aligned in various directions, an approximative description of the diffusive medium as a quasi-continuum seems to be justified. The appropriate equation for the recoil atoms concentration is then

$$\frac{\partial c_r}{\partial t} = D_d\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right)c - \lambda c + \zeta_r \epsilon \tag{17}$$

where D_d is the mean diffusion coefficient of the quasi-continuum. D_d clearly has to be dependent on ϵ and on temperature, i.e.

$$D_d(T) = d_d \epsilon \exp(-E_{dd}/RT) \tag{18}$$

where d_d is an appropriate constant and E_{dd} is the mean activation energy of the diffusion jumps. Assuming, again, the first order kinetics for the dissipation of the continuous defects, eqn. (18) gives

$$D_d(T) = d_d \epsilon_0 \exp\left[-E_{dd}/RT - \frac{p_d}{\kappa}\int_{T_0}^{T} \exp(-E_{rd}/R\sigma)\mathrm{d}\sigma\right] \tag{19}$$

where p_d, E_{rd} are the constants of the kinetics of the defects' dissipation.

Returning now to eqn. (17) and taking the boundary conditions $\partial c(0, r)/\partial t = 0$, $c(t, 0) = 0$ and $\partial c(t, \rho_r)/\partial r = 0$, we obtain the solution

$$\begin{aligned} c(t,r) = \frac{2}{\rho_r}\, e^{-\lambda t} \sum_{n=\theta}^{\infty} \Bigg\{ &\exp\left(-\frac{n^2\pi^2}{\rho_r^2}\tau_{d,t}\right) \cos\left[\beta_n \frac{r_p + \rho_r - r}{r_p + \rho_r}\right] \\ &\times \int_{r_p}^{r_p+\rho_r} \phi(s) \cos\left[\beta_n \frac{r_p + \rho_r - s}{r_p + \rho_r}\right]\mathrm{d}s + \cos\left[\beta_n \frac{r_p + \rho_r - r}{r_p + \rho_r}\right] \\ &\times \int_0^t \epsilon\zeta_r \exp\left[-\frac{\pi^2 n^2}{\rho_r^2}(\tau_{d,t} - \tau_{d,\chi})\right] \int_{r_p}^{r_p+\rho_r} \cos\left[\beta_n \frac{r_p + \rho_r - s}{r_p + \rho_r}\right]\mathrm{d}s\,\mathrm{d}\chi \Bigg\} \end{aligned} \tag{20}$$

where

$$\tau_{d,x} = \int_0^x D_d(\chi)\mathrm{d}\chi \tag{21}$$

and

$$\phi(s)=\frac{\epsilon\zeta_r}{\lambda}\left\{1-\frac{K_0(b)I_0\left[is(\lambda/D_{d,0})^{1/2}\right]-I_0(b)K_0\left[is(\lambda/D_{d,0})^{1/2}\right]}{I_0(a)K_0(b)-I_0(b)K_0(a)}\right\} \tag{22}$$

where $a=ir_p(\lambda/D_{d,0})^{1/2}$ and $b=i(r_p+\rho_r)(\lambda/D_{d,0})^{1/2}$ and I_0, K_0 are the modified Bessel (i.e., McDonald) functions of the first and the second kind, respectively.

From this, the part of the creation function due to diffusion is

$$\begin{aligned}\zeta_d(T)=\frac{4\pi r_p}{\rho_r}D_d(T)\,e^{-\frac{\lambda(T-T_0)}{\kappa}}\\ \times\sum_{n=0}^{\infty}\left\{\exp\left(-\frac{n^2\pi^2}{\rho_r^2\kappa}\tau_{d,t}\right)\int_{r_p}^{r_p+\rho_r}\phi(s)\cos\left[\beta_n\frac{r_p+\rho_r-s}{r_p+\rho_r}\right]ds\right.\\ \left.+\int_{T_0}^{T}\epsilon(\chi)\zeta_r\exp\left[\frac{\lambda}{\kappa}\chi-\frac{n^2\pi^2}{\rho_c^2\kappa}(\tau_{d,t}-\tau_{d,\chi})\right]d\chi\right\}\end{aligned} \tag{23}$$

In the case of the homogeneous distribution of the parent isotope, ζ_r is simply $\Lambda_T c_T$.

Taking into account both assumed mechanisms of the escape of recoil atoms into the pore, the new creation function $\zeta(T)$ for eqn. (3) is

$$\zeta(T)=(1-\epsilon)\zeta_e(T)+\zeta_d(T) \tag{24}$$

where $\zeta_e(T)$ and $\zeta_d(T)$ are defined in eqns. (16) and (23), respectively. Using these expressions, we assume implicitly the irreversibility of the recoil atoms' escape. This approximation should be justified by the extremely low probability of the new penetration of the escaped atoms through the potential barrier of the wall and by their much easier mobility through the pore. The order of this approximation is, in fact, the same as that which is implied by setting the concentration of the gas to zero at the outer end of the pore.

Emanation rate due to inert gas diffusion in the solid matrix

The diffusion of the inert gas in the solid matrix and through the outer surface of the body was neglected by our original model [3]. The comparison of the simulated ETA curves with the experimental ones showed, however, a rather serious discrepancy at higher temperatures. Therefore, we include it into the modified version of the model.

In this case, the diffusion of the inert gas in a solid spherical body is described by the following equation

$$\frac{\partial c_r(r,t)}{\partial t}=D_s\left[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right]c(r,t)-\lambda c(r,t)+\eta_r(t) \tag{25}$$

Equation (25) is, of course, a slight idealisation in the implicit assumption of the spherical symmetry. As the distortion of the symmetry by the influence of the pores is rather slight at temperatures at which the gas diffusion in the solid matrix contributes significantly to the total emanation rate, it is neglected in this version of the model. In this case, the radial distribution function of the intermediate nuclide (assuming the constant distribution of the parent nuclide $c_T(r)$ and the radioactive equilibrium, i.e., the steady state) is, in the case of $c_T(r) = c_T$

$$c_R(r) = \begin{cases} \dfrac{\Lambda_T}{\Lambda_R} c_T & r \in \langle 0, R_b - \rho_R \rangle \qquad (26a) \\[2ex] \dfrac{\Lambda_T}{\Lambda_R} c_T \dfrac{R_b^2 - (r - \rho_R)^2}{4 r \rho_R} & r \in \ (R_b - \rho_R, R_b \rangle \qquad (26b) \end{cases}$$

and, in the case of $c_T(r) = c_T$, $r \in \langle R_b - \Delta,\ R_b \rangle$, and $c_T(r) = 0$, $r \in \langle 0, R_b - \Delta)$

$$c_R(r) = \begin{cases} 0 & r \in \langle 0, R_b - \rho_R \rangle \qquad (26c) \\[2ex] \dfrac{\Lambda_T c_T}{\Lambda_R} \dfrac{\Delta(2R_b - \Delta)}{4 r \rho_R} & r \in \ (R_b - \rho_R, R_b \rangle \qquad (26d) \end{cases}$$

where Δ is the thickness of the surface layer containing the parent nuclide. Now, under the given assumptions, the creation function of the gas $\eta_r(r)$ in eqn. (25) is

$$\eta_r(r) = \frac{\Lambda_R}{r^2} \int_{r - \rho_r}^{x} \rho^2 c_R(\mu) \mathrm{d}\mu \qquad (27)$$

where $c_r(\mu)$ is the appropriate function from the equation set (26a) to (26d) and x is either $r + \rho_r$ or R_b. With such function, the solution of eqn. (25) is

$$c(r, t) = \frac{2}{R_b} \mathrm{e}^{-\lambda t} \times \sum_{n=0}^{\infty} \sin\left(\beta_n \frac{R_b - r}{R_b} \right) \left\{ \exp\left(-\frac{n^2 \pi^2}{R_b^2} \tau_t \right) \int_0^{R_b} \phi(s) \sin\left(\beta_n \frac{R_b - s}{R_b} \right) \mathrm{d}s + \int_0^t \frac{\mathrm{e}^{\lambda \chi}}{D(\chi)} \exp\left[-\frac{\pi^2 n^2}{R_b^2} (\tau_t - \tau_\chi) \right] \int_0^{R_b} \eta_r(s) \sin\left(\beta_n \frac{R_b - s}{R_b} \right) \mathrm{d}s \mathrm{d}\chi \right\} \qquad (28)$$

where

$$\tau_x = \int_0^x D_s(\chi) \mathrm{d}\chi \qquad (29)$$

and the diffusion coefficient $D_s(T)$ is assumed to be dependent on temperature only, namely

$$D_s(T) = D_{s0}\exp(-E_s/RT) \tag{30}$$

Under the initial steady state and with the approximation (which allows the continuous description of the process for the whole sphere and which is quite good for the relevant outer region)

$$\eta_r(r) = \Lambda_T c_T \left[1 - \beta \exp\left(-\frac{R_b - r}{\rho_R}\right)\right],$$

where $\beta = 10^{-15}/\rho_r\rho_R$, the initial function $\phi(r) = c(r, 0)$ is

$$\phi(r) = \frac{1}{\omega}\left\{\left[(\psi_1 R_b - \psi_2)\frac{\sinh(\omega r)}{\sinh(\omega R_b)} - \psi_2\right]\frac{1}{r} + \psi_1\right\} \tag{31}$$

with

$$\psi_1 = \frac{\Lambda_T c_T}{\omega} + \frac{2\beta\rho_R^2\omega}{(1+\rho_R\omega)(1-\rho_R\omega)} \tag{32a}$$

and

$$\psi_2 = \frac{4\beta\rho_R^3\omega}{(1+\rho_R\omega)^2(1-\rho_R\omega)^2} \tag{32b}$$

where $\omega = \sqrt{\lambda/D_s(T_0)}$.

From these expressions, we get for the diffusion part of the emanation rate due to the diffusion in the solid matrix

$$\begin{aligned}\epsilon_s = {} & 4\pi\left(2R_b - \frac{N_p r_p^2}{R_b}\right) D_{s0}\exp(-E_s/RT - \lambda\Delta T/\kappa) \\ & \times \sum_{n=0}^{\infty}\Bigg\{\exp\left(-\frac{n^2\pi^2}{\kappa R_b^2}\tau_T\right)\int_0^{R_b}\phi(s)\sin\left(\beta_n\frac{R_b - s}{R_b}\right)\mathrm{d}s \\ & + \Lambda_T c_T\int_{T_0}^{T}\exp\left\{E_S/R\chi + \frac{1}{\kappa}\left[\lambda\kappa - \frac{\pi^2 n^2}{R_b^2}(\tau_T - \tau_\chi)\right]\right\} \\ & \times \int_0^{R_b}\left[\frac{1}{2} - \frac{s^2 - (R_b^2 - \rho_r^2)}{4\rho_r s}\right]\sin\left(\beta_n\frac{R_b - s}{R_b}\right)\mathrm{d}s\,\mathrm{d}\chi\Bigg\}\end{aligned} \tag{33}$$

RESULTS

In the computations presented here, the labelling of the solid sample by ^{228}Th is supposed, giving rise to the emanation of ^{220}Rn as follows: $^{228}\mathrm{Th} \xrightarrow{\alpha} {}^{224}\mathrm{Ra} \xrightarrow{\alpha} {}^{220}\mathrm{Rn}$. The following values of the parameters were used, if not specified otherwise: $R_b = 10^{-4}$ m, $\rho_R = 3.95 \times 10^{-8}$ m, $\rho_r = 4.17 \times 10^{-8}$ m, $r_{p0} = 10^{-7}$ m, $l = 5 \times 10^{-5}$ m, $N_p = 4 \times 10^5$, $K_p = 10^{13}$ K s^{-1}, $E_p = 160$ kJ mol^{-1}, $K_e = 0.01$ K s^{-1}, $E_e = 140$ kJ mol^{-1}, $K_r = 10^{11}$ K s^{-1}, $E_{rd} = 160$ kJ mol^{-1}, $D_{s0} = 1.0$, $E_s = 280$ kJ mol^{-1}. In all cases, the emanation rate is in units relative to the value $\Lambda_T c_T = 1.0$.

Comparison of different levels of the model

Figure 1 shows the following comparison of the curves $\epsilon(T)$ computed with the above listed values of the parameters and using the following levels of the model: (i) the original model (curve 1); (ii) the modified model taking into account the fractional escape of the recoil atoms through the systematic defects of both kinds, $\epsilon_0 = 0.1$ (curve 2); (iii) model (ii) also taking into account the inert gas diffusion in the solid matrix through the outer surface of the body. Also given in Fig. 1 is an example of the experimental ETA curve obtained when analysing silica gel labelled by ^{228}Th. It is obvious that both modifications (ii) and (iii) are needed for the model to correspond

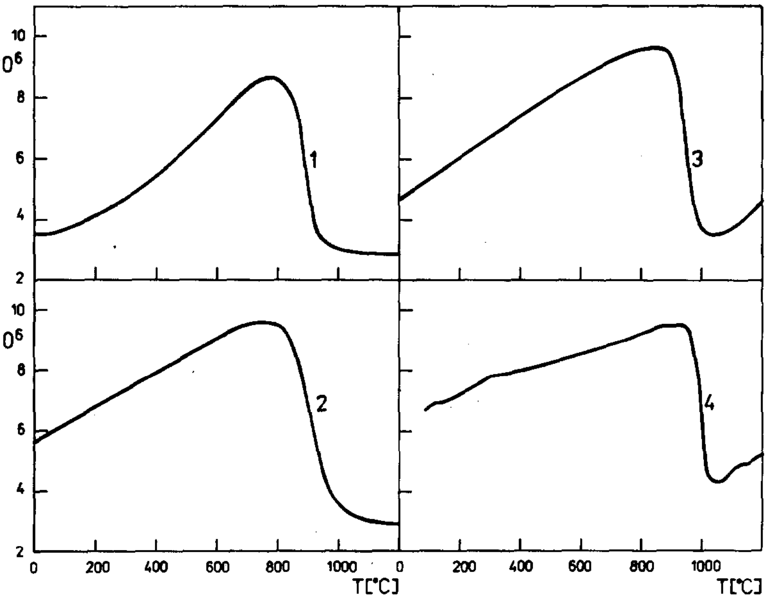

Fig. 1. Comparison of temperature dependence of the emanation rate $\epsilon(T)$ under constant heating rate $\kappa = 0.1$ K s^{-1}: (1) theoretical curve corresponding to the original model, with $r_{p0} = 10^{-7}$ m, $R_b = 10^{-4}$ m, $l = 5 \times 10^{-5}$ m, $N_p = 4 \times 10^5$, $K_p = 10^{13}$ K s^{-1}, $E_p = 160$ kJ mol^{-1}; (2) theoretical curve of the model taking into account the escape of recoil atoms via continuous defects, with additional parameters $K_e = 0.01$ K s^{-1}, $E_e = 140$ kJ mol^{-1}, $K_{rd} = 10^{11}$ K s^{-1}, $E_{rd} = 160$ kJ mol^{-1}; (3) theoretical curve of the fully improved model also taking into account the gas diffusion in the solid matrix, with additional parameters $D_{s0} = 10^7$, $E_s = 280$ kJ mol^{-1}; (4) the experimental ETA curve of silica gel labelled by ^{228}Th under the same conditions.

sufficiently with experimental reality, though the inclusion of the diffusion in the solid only affects the later part of the computed curve.

The effect of the radius r_{p0} *of the pores*

Figure 2 shows the $\epsilon(T)$ curves computed from the fully modified model for the pore radii $r_{p0} = 2 \times 10^{-7}$, 1×10^{-6}, 5×10^{-6} and 2.5×10^{-5} m (the last of which is somewhat unrealistic and is included for illustration only). It can be seen that the growth of the initial pore radius affects the ETA curve in the low-temperature range. The initial values of $\epsilon(T)$ increase whereas the slope of the curve tends to fall with increasing r_{p0}. The differences in the decrease of the curve in the range 800 to 900 °C as shown in Fig. 2 may be an artifact of the supposed kinetics of the pore sintering, which remains to be clarified by special experiments.

The effect of the heating rate

Figure 3 shows the curves computed from our modified model for the following values of the linear heating rate $\kappa = 0.05$, 0.20, 0.80 and 3.20 K s^{-1}. As can be seen, the pseudolinear part of the curve tends to an exponential form and, by higher heating rates, new maxima can be formed on the curve. This fact has to be taken into account in the interpretation of ETA experimental curves: not every irregularity indicates some distinct

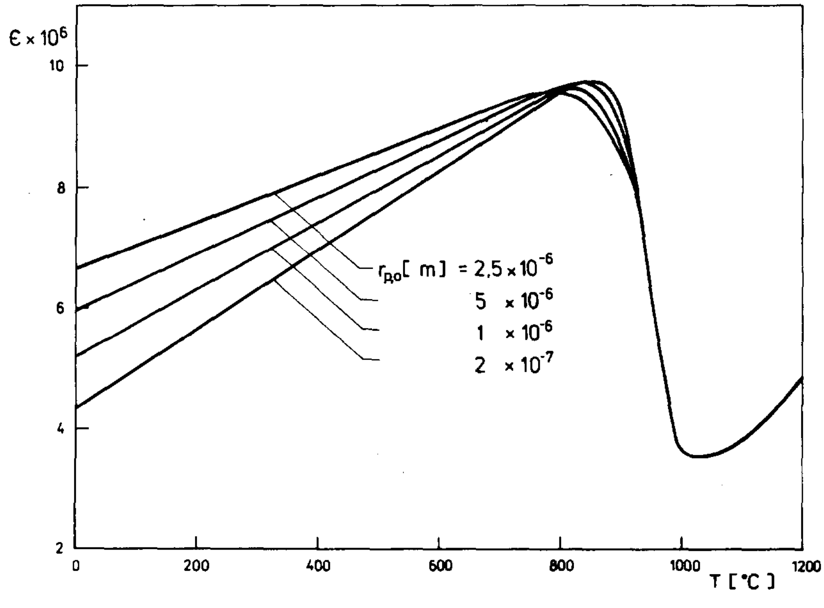

Fig. 2. The effect of the pore radius on the temperature dependence of the emanation rate $\epsilon(T)$; for other parameters see Fig. 1.

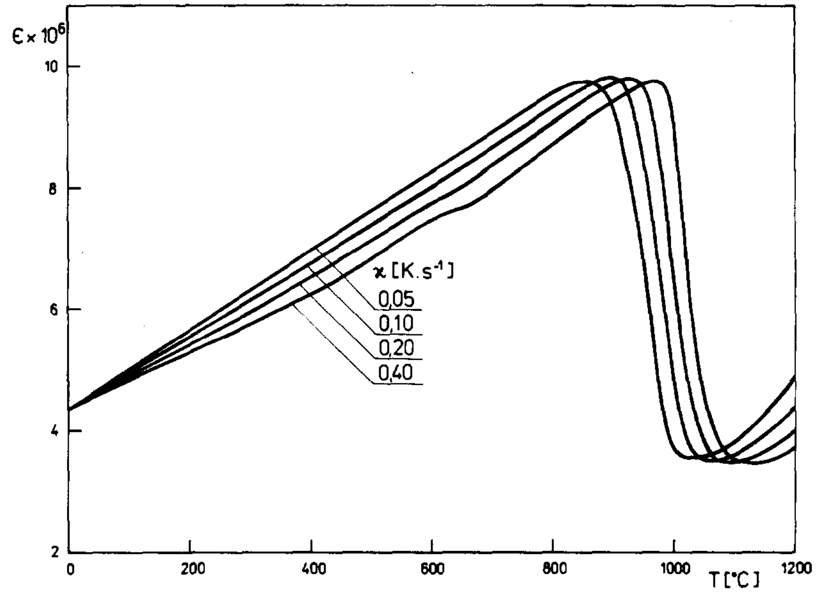

Fig. 3. The effect of the heating rate κ on the temperature dependence of the emanation rate $\epsilon(T)$; for other parameters see Fig. 1.

physical process. Additionally, the increase of the heating rate clearly leads to the displacement of the maximum as well as of the minimum of the curve to higher temperatures. As previously shown [7] in a very simplified quasi-

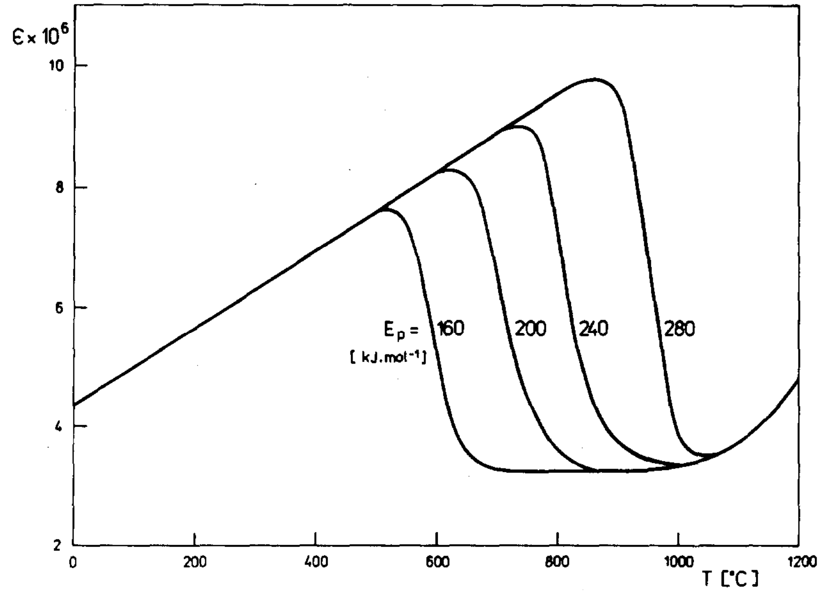

Fig. 4. The effect of the activation energy E_p of the pore sintering on the temperature dependence of the emanation rate $\epsilon(T)$; for other parameters see Fig. 1.

isothermal model, this feature can be used for the estimation of the activation energy of the sintering of the pores.

The effect of the activation energy E_p *of the pore sintering*

In Figure 4 the dependence of the form of the ETA curve on the value of the activation energy of pore sintering E_p is illustrated for $E_p = 160$, 200, 240 and 280 kJ mol^{-1}. The increase in E_p clearly shifts the first maximum of the curve to a higher temperature and simultaneously increases the value of $\epsilon(T)$ at the maximum. The further part of the curve depends, among other factors, on the relationship of E_p to E_s; with the increase of $(E_s - E_p)$, the first minimum of the curve becomes more prominent and could, in some cases, even lead to a plateau in the curve.

The effect of the increase of log K_p (K_p being the other constant characterizing the kinetics of the pore sintering) is qualitatively the same as that of E_p and has been illustrated elsewhere [7]. This is, once again, an example of the "compensation effect" popular in thermal analysis, which is, however, brought about simply by the supposed Arrhenius temperature dependence of the constant of kinetics and not by some alleged peculiarity of the process.

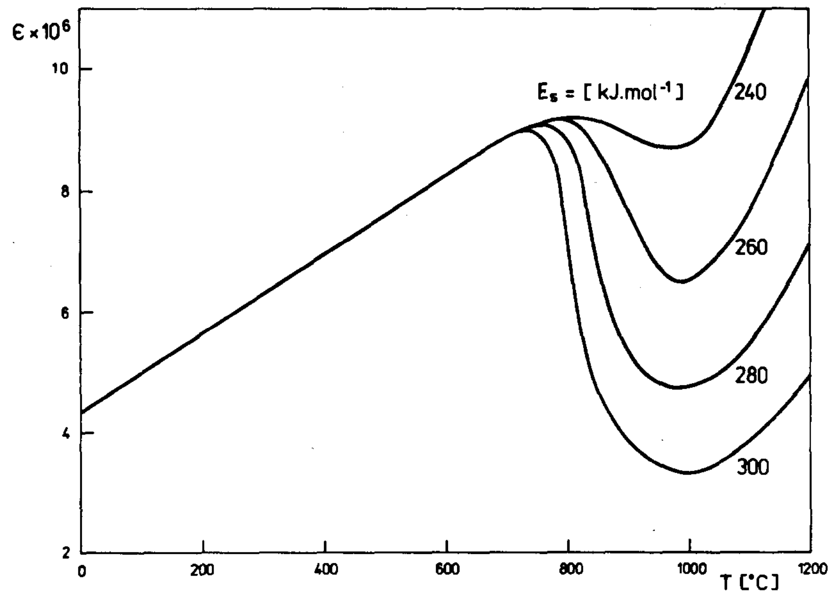

Fig. 5. The effect of the activation energy E_s of the gas diffusion in the solid matrix on the emanation rate $\epsilon(T)$; for other parameters see Fig. 1.

The effect of the activation energy E_s *of inert gas diffusion in the solid matrix*

As indicated in the foregoing paragraph, the interplay of the values of E_p and E_s has a pronounced effect on the overall form of the curve. This is illustrated by Fig. 5, where E_p is fixed at the value 200 kJ mol^{-1} and $E_s = 200$, 220, 240 and 260 kJ mol^{-1}. The minimum of the curve is clearly shifted in both directions. Hence the position of the maximum can serve as the criterion of E_p whereas from the position of the minimum the value of $E_s - E_p$ can be, in principle at least, evaluated. Owing to the complexity of the mathematical model, however, no direct method for such an evaluation seems to be available; the only apparent way is the computer optimalization of the parameters by curve fitting, which is, unfortunately, a rather tedious task.

The effect of the parameters, characterizing the defectivity of the solid

The underlying physical idea of the mathematical formulation of the function ζ_d is the connection between the porosity of the sample (which is expressed by the values of N_p and r_p) and the defectivity of the solid in the immediate vicinity of the pores. The probability of such connection can be inferred from various possible mechanisms of the pore formation. Two different cases should be considered here, however. A point or cluster defect as such is, in contrast to the higher-mobility sites, rather a trap for the migrating atom [5]; a continuous defect such as a micro- or submicropore or a linear defect, on the other hand, can serve as a high-mobility escape path. The parameter α, which we introduced into the function ζ_d to express statistically the fraction of such defects, can actually have a somewhat ambiguous meaning. As the mathematical form of ζ_d under our quasi-continuum approximation describes any diffusion in the cylindrical geometry, quite another situation can be expressed by a suitable choice of the activation energy E_{dd} and the initial value of the defectivity parameter ϵ_0 in eqn. (19), namely the competition between interstitial diffusion and the slower diffusion via defect migration. In this case, however, the higher value of ϵ_0 means a lower defectivity of the solid and the exponential rise of ϵ with temperature need not be as general since the usual restoration of the solid matrix by higher temperatures can be accompanied by the coalescence of small defects into bigger clusters with lower mobility. Such ambiguity of the model can be valued both positively and negatively but can be resolved by the use of the model in an unambiguous situation—namely, as in this case, for the microporous solids.

The dependence of the ETA curves on the parameters ϵ_0 and E_{dd}, characterizing the defect state of the solid, is shown in Figs. 6 and 7, respectively. In Fig. 6 the effect of ϵ_0 is illustrated for $\epsilon_0 = 0.1$, 0.2 and 0.3 and in Fig. 7 the effect of E_{dd} is shown for $E_{dd} = 80$, 100, 120 and 140 kJ

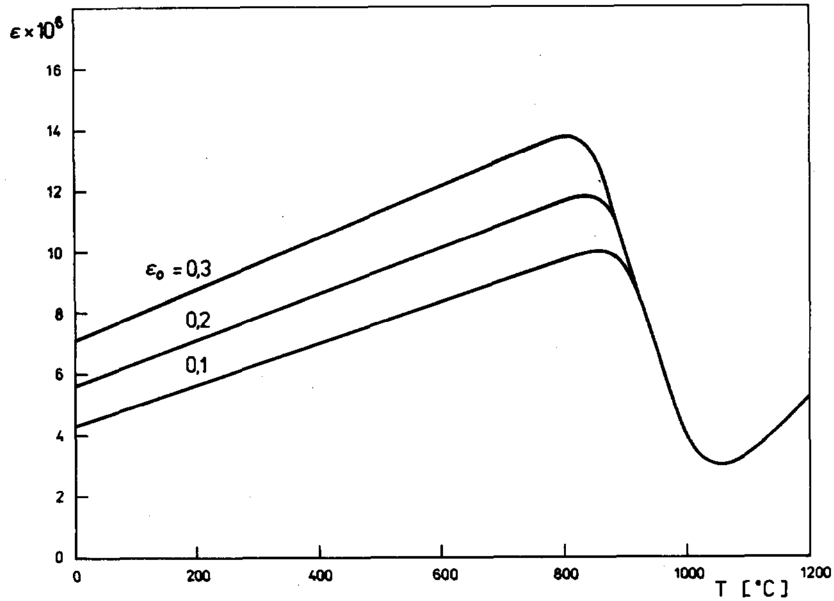

Fig. 6. The effect of the defectivity parameter ϵ_0 on the temperature dependence of the emanation rate $\epsilon(T)$; for other parameters see Fig. 1.

mol^{-1}. It can be seen that higher ϵ_0 values as well as lower E_{dd} values lead to higher initial ϵ values as well as to the higher slope of the first part of the ETA curve. The form of this part of the ETA curve is, however, affected by

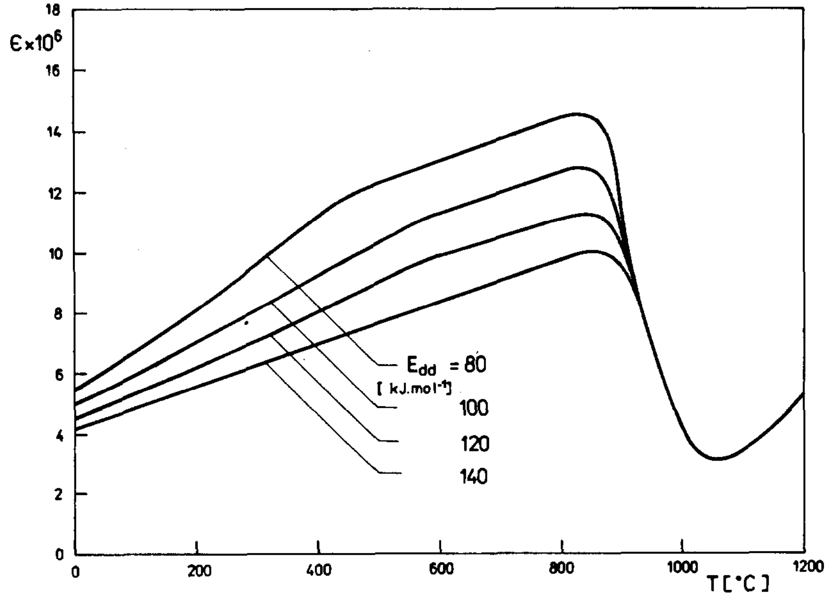

Fig. 7. The effect of the activation energy E_{dd} of the diffusional escape of recoil atoms on the temperature dependence of the emanation rate $\epsilon(T)$; for other parameters see Fig. 1.

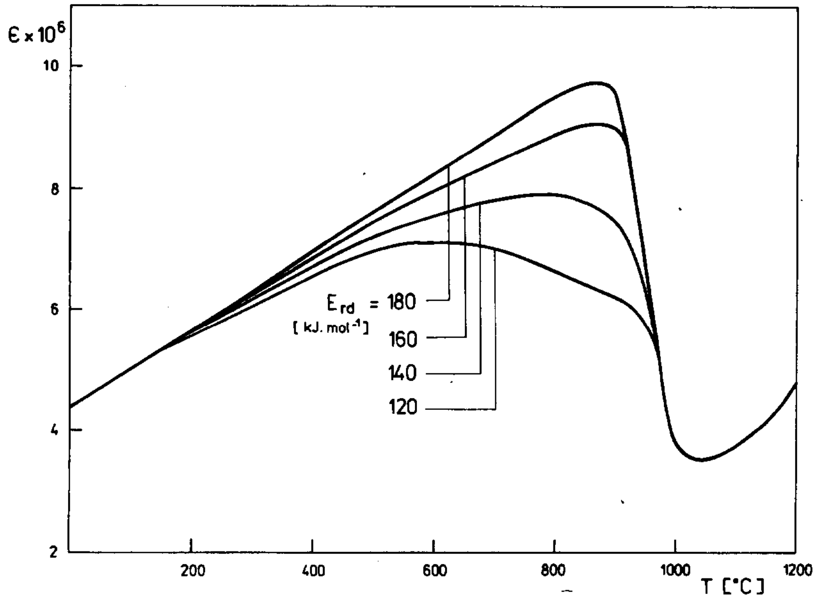

Fig. 8. The effect of the activation energy E_{rd} of matrix restoration on the temperature dependence of the emanation rate $\in (T)$; $E_{dd} = 100$ kJ mol^{-1}; for other parameters see Fig. 1.

the value of the activation energy of the matrix restoration E_{rd} as well. This is illustrated in Fig. 8 where E_{rd} is varied (120, 140, 160 and 180 kJ mol^{-1}) with E_{dd} constant at 100 kJ mol^{-1}. As it can be seen, the pseudolinearity of the first part of the ETA curve is, at least in the present model, brought about by the interplay of the increasing mobility of the recoil atoms and of the closing of the escape paths.

CONCLUSIONS

The mathematical model of inert gas release from a porous solid suggested earlier has been improved. The mechanism of inert gas diffusion in the solid matrix and of the inert gas release during the annealing of defects under non-isothermal conditions has been taken into account in the improved model.

The material constants suggested in the model describe the physical state of the solid, especially its defect state, the kinetics of the annealing of defects and of the pore sintering.

The computer simulations of the model have shown sufficient flexibility of the model to meet the most important features of the ETA experimental curves. The detailed comparison of the theoretical model with the experimental curves for various porous materials will be given in Part III of this series.

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