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THEORY OF EMANATION THERMAL ANALYSIS.
I. MATHEMATICAL MODEL FOR INERT GAS RELEASE FROM POROUS SOLIDS

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ABSTRACT

The expression for the emanation rate due to recoil and to the diffusion of inert gas in pores is given for a solid spherical body labelled by the appropriate parent nuclides. This model describes a solid with radial cylindrical pores of both uniform and general distribution sizes The derived expressions describe the behaviour of inert gas release from porous solids during non-isothermal treatment This new approach avoids the usual errors of quasi-isothermal approximation.

INTRODUCTION

Emanation thermal analysis (ETA) [1,2], in spite of its wide use, has lacked adequate theory. The most commonly used mathematical model based on the early work by Flugge and Zimens [3] has been proposed to describe the course of the release of inert gas from a compact spherical body under isothermal conditions. Its shortcomings appear to be serious [4,5] in the case of markedly porous materials over moderate temperature ranges, especially under a substantial rate of linear heating. There appear to be two main reasons for this: (i) the major part of the emanation rate under such conditions is not due to the recoil of inert gas (ϵ_R) or the diffusion through the solid (ϵ_D) but is due to the fast diffusion through the pores (ϵ_P); (ii) the use of the quasi-isothermal model in the case of ETA is too crude: the main effects of ETA are probably brought about by the distortion of the steady state, the assumption of which is crucial for the quasi-isothermal approximation.

The aim of this study is therefore to explore the possibilities of a more adequate theoretical model. We start with a rather simple case of a spherical

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body with radial cylindrical pores impregnated or otherwise labelled by a long-lived parent radionuclide (e.g., ^{228}Th). Even in this case, not all necessary physical information is available so that some assumptions have to be made. In the first part of this study we present the derivation of the model, in the second part, to appear later, its exploration by computer simulation.

THEORY

For a homogeneous spherical body of radius R_b with N_p pores of a uniform cylindrical shape of radius r_p and length l, all pores should reach the outer surface in the radial direction (see Fig. 1). The body contains a long-lived parent radionuclide (e.g., ^{228}Th) either impregnated on its outer as well as on its inner surface or distributed homogeneously in the solid, decaying to a daughter secondary nuclide (e.g., ^{224}Ra) and subsequently to a radioactive inert gas (e.g., ^{220}Rn). The recoil ranges of the secondary nuclide (^{224}Ra) and of the inert gas (^{220}Rn) in the solid are ρ_R and ρ_r, respectively, and the same in the phase of pores ρ'_R and ρ'_r, respectively.

The emanation rate * from such a body can be expressed as the sum of the parts due to the recoil (ϵ_R), the diffusion through the pores (ϵ_P) and the diffusion through the solid (ϵ_D)

$$\epsilon = \epsilon_R + \epsilon_P + \epsilon_D \tag{1}$$

The last term of eqn. (1) is negligible in some cases, for example, in inorganic ionic crystals over a moderate temperature range. Therefore, to simplify the solution, the diffusion term ϵ_D will not be taken into account.

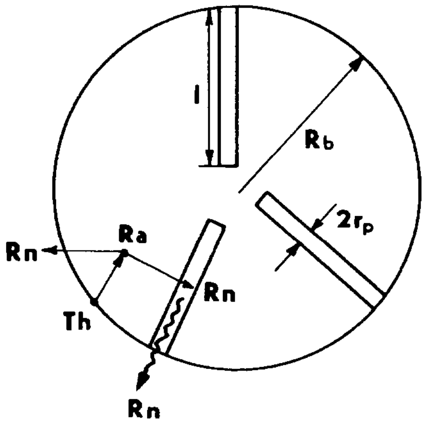

Fig 1 Scheme of the radon release by recoil and diffusion from a porous solid grain labelled with ^{228}Th and ^{224}Ra parent nuclides (for the symbolds see text)

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* Emanation rate is the rate of release of inert gas from the solid

Distribution of the secondary nuclide and the creation function of inert gas in pores

The instant concentration of the secondary nuclide in the volume element with its centre at the point x follows the differential equation

$$\frac{\delta c_{\mathrm{R}}(x_1 t)}{\delta t} = \Lambda_{\mathrm{T}} \int_0^{\rho_{\mathrm{R}}} \int_0^{2\pi} \int_0^{2\pi} c_{\mathrm{T}}(r, \varphi, \vartheta, t) p(r, \varphi, \vartheta) \, \mathrm{d}r \mathrm{d}\varphi \mathrm{d}\vartheta - \Lambda_{\mathrm{R}} c_{\mathrm{R}}(x, t) \tag{2}$$

where the origin of the polar coordinates is at x, $c_{\mathrm{T}}(r, \varphi, \vartheta, t)$ is the instant concentration of the parent nuclide, $p(r, \varphi, \vartheta)$ is the probability that the atom emitted from the point (r, φ, ϑ) will reach the point x, and Λ_{T} and Λ_{R} are the decay constants of the parent and secondary nuclide, respectively.

For a sufficiently large difference between Λ_{R} and Λ_{T}, we may assume the radioactive equilibrium, i.e., $\delta c_{\mathrm{R}}(x, t)/\delta t = 0$. The concentration $c_{\mathrm{R}}(x, t)$ at the distance x from the pore wall is then

$$c_{\mathrm{R}}(x, t) = \frac{\Lambda_{\mathrm{T}} c_{\mathrm{T}}}{\Lambda_{\mathrm{R}}} \chi(x) \tag{3}$$

where the geometrical factor $\chi(x)$ (neglecting, for simplicity, the curvature of the pore wall and the slowing-down of the recoil atoms by the pore medium) is

$$\chi(x) = \frac{1}{2\rho_R} \left(1 + \frac{\rho'_{\mathrm{R}} - 2r_{\mathrm{p}}}{\rho'_{\mathrm{R}}} \right) \tag{4a}$$

for the surface impregnation by the parent nuclide and

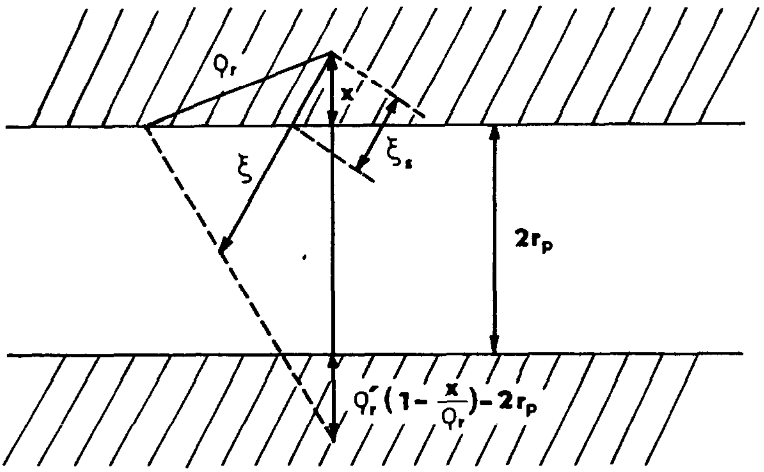

Fig. 2. Calculation scheme of the range of recoil atoms in the porous solid (for the symbols see text).

$$\chi(x) = 1 \tag{4b}$$

for the homogeneous distribution of the parent isotope.

The probability of emitting an atom by recoil above the pore wall from the depth x is (neglecting the curvature)

$$p_{1x} = \frac{2\pi(\rho_r - x)}{4\pi\rho_r^2} = \frac{\rho_r - x}{\rho_r^2} \tag{5}$$

The probability p_{2x} that the emitted atom will hit the pore wall again is rather complicated even under the assumptions already made. As may be seen from Fig. 2, the range ξ of the recoil atoms to be considered is

$$\xi = \rho_r'\left(1 - \frac{\xi_s}{\rho_r}\right) + \xi_s \tag{6}$$

where ξ_s is the length of the trajectory in the solid. Approximating the surface of eqn. (6) by a cone, the probability p_{2x} is

$$p_{2x} = \left(1\frac{\eta}{\rho_r - x}\right)^2 \tag{7}$$

where

$$\eta = \frac{2r_p\rho_r}{\rho_r'} \tag{7a}$$

The expression (7) does not, however, express the true probability that the emitted atom will be lost for the pore diffusion. There is clearly some probability that such an atom will escape again along its own trajectory by diffusion, which depends on the extent of the matrix disorder and on temperature. It therefore seems reasonable to make a correction to eqns. (7) in the following way

$$p_{2x} = \left(1 - \frac{\eta}{\rho_r - x}\right)^2 [1 - p_0 \exp(-E_e/RT)] \tag{7b}$$

where E_e is an activation energy and p_0 is a phenomenological coefficient $\leqslant 1$. Under such assumptions the probability that the recoil atom will enter the pore is

$$p_x = p_{1x}(1 - p_{2x}) = \frac{\rho_r - x}{\rho_r^2}\left\{1 - \left(1 - \frac{\eta}{\rho_r - x}\right)^2 [1 - p_0 \exp(-E_e/RT)]\right\} \tag{8}$$

Consider a typical pore with $r_p \ll l$ and $r_p < k_f$, k_f being the free range of the atoms in the pore medium under given conditions. In such a case, the radial homogenization of the inert gas in the pore will be much faster than the longitudinal diffusion and the creation function $\zeta(T)$ of the inert gas in the pore can be considered to be radially independent

$$\zeta(T) = A\Lambda_R \int_0^{\rho_R} p_x c_R(x)\,\mathrm{d}x \tag{9}$$

where A is a factor depending of the units of c_T, being $A = r_p^{-1}$ if c_T is in surface units. From eqns. (3), (8) and (9)

$$\zeta(T) = A\Lambda_T c_T \chi(x)\gamma\left[\left(1 - \frac{\gamma}{2}\right) - \left\{1 - \frac{\gamma}{2} - \frac{4r_p}{\rho_r'}\left[1 - \frac{r_p\gamma}{\rho_r'}\ln(1-\gamma)\right]\right\}\right.$$
$$\left.\times\left[1 - p_0\exp(-E_e/RT)\right]\right] \tag{10}$$

where $\gamma = \rho_R/\rho_r$.

Pore permeability and the diffusion coefficient of inert gas diffusion in pores

The salient fact on which our model is mainly based is the generally observed increase of the emanation rate followed by its rather sharp decrease in a temperature range mostly from 0.3 to 0.5 T_{melting}. The simplest explanation of this is a sintering process by which the pores are gradually closed, decreasing their permeability to the diffusing inert gas. Assuming the validity of the Knudsen expression for the diffusion coefficient

$$D_p(T) = \sqrt{\frac{8R}{\pi M}}\, T^{1/2} r_p \tag{11}$$

some expression is required for $r_p(T)$, i.e., some reliable kinetics of the sintering process. Unfortunately, there is no certainty in this field as yet (cf., ref. 6). Therefore, we shall proceed in the following way.

Should the sintering proceed either by evaporation–condensation, or by diffusion or by plastic flow, its rate will be proportional to the inner surface area of the pore and, in addition, it will depend on the pore radius. Thus, the simplest possible phenomenological equation of any reliability, describing the change of the pore volume V_p, is

$$-\mathrm{d}V_p/\mathrm{d}t = k_p S_p r_p^{\alpha} \tag{12}$$

where k_p is some rate constant with the usual exponential dependence on temperature (the exponent being formed by the activation energy of self-diffusion and/or by the evaporation heat), S_p is the inner surface of the pore and α is some exponent. Taking $\alpha = 1$, the following expression follows from eqn. (12)

$$-\frac{\mathrm{d}r_p}{\mathrm{d}T} = \frac{K_p}{\kappa} r_p \exp(-E_p/RT) \tag{13}$$

where κ is the linear heating rate and K_p and E_p are the usual coefficients of the Arrhenius function. From eqn. (13), the diffusion coefficient [see eqn. (11)] takes the form

$$D_p(T) = r_{p0}\sqrt{\frac{8R}{\pi M}}\, T^{1/2}\exp\left[-\frac{K_p}{\kappa}\int_{T_0}^{T}\exp(-E_p/RT)\mathrm{d}T\right] \tag{14}$$

It can be readily seen that the value of eqn. (14) has a maximum, its location being

$$T_{\max} = \frac{\kappa}{K_{\mathrm{p}}} \exp(E_{\mathrm{p}}/RT)$$

The appropriateness of eqn. (14) depends on the validity of eqn. (13) and of the correct value of α. It will be seen, however, that the general conclusions of this study are open to a further improvement in this field.

Emanation rate ϵ_P

To derive the expression for the part of the emanation rate caused by the pore diffusion, the corresponding equation of diffusion must be solved. Under the assumptions already made, the concentration of the inert gas in the pore must follow the differential equation

$$\frac{\delta c(r, x, t)}{\delta t} = D_{\mathrm{p}}(+)\left[\frac{\delta^2}{\delta r^2} + \frac{1}{r}\frac{\delta}{\delta r} + \frac{\delta^2}{\delta x^2}\right] c(r, x, t) - \lambda c(r, x, t) + \zeta(t) \quad (15)$$

where λ is the decay constant of the inert gas, D_{p} is the diffusion coefficient and $\zeta(t)$ is the creation function of this gas. Considering, however, the function ζ to be independent of r (see earlier), both $\delta c/\delta r$ and $\delta^2 c/\delta r^2$ are vanishing and thus take the form

$$\frac{\delta c(x, t)}{\delta t} = D_{\mathrm{p}}(t)\frac{\delta^2 c(x, t)}{\delta x^2} - \lambda c(x, t) + \zeta(t) \quad (16)$$

with the boundary conditions

$$c(x, 0) = \varphi(x) \quad (16a)$$

$$c(0, t) = 0 \quad (16b)$$

$$\delta c(l, t)/\delta x = 0 \quad (16c)$$

the last of which precludes the diverging behaviour of $c(x, t)$. It seems reasonable to assume the steady state at the start of the experiment, i.e., $\delta c(x, 0)/\delta t = 0$; thus

$$D_{\mathrm{p}}(0)\frac{\delta^2 c(x, 0)}{\delta x^2} - \lambda c(x, 0) + \zeta(0) = 0 \quad (17)$$

with the boundary conditions analogous to eqn. (16b,c). The solution to eqn. (17) is straightforward, giving

$$c(x, 0) = \varphi(x) = \frac{\zeta(0)}{\lambda}\left\{1 - \frac{\sinh\left[(l - x)\sqrt{\lambda/D_{\mathrm{p}}(0)}\right]}{\sinh\left[l\sqrt{\lambda/D_{\mathrm{p}}(0)}\right]}\right\} \quad (18)$$

Returning to eqn. (16), the solution can be expected in the form

$$c(x, t) = v(x, t) + w(x, t) \tag{19}$$

where $v(x, t)$ is the solution to the homogeneous equation

$$\frac{\delta v(x, t)}{\delta t} = D(t)\frac{\delta^2 v(x, t)}{\delta x^2} - \lambda v(x, t) \tag{20}$$

with the boundary conditions analogous to eqn. (16a, b, c), and $w(x, t)$ corresponds to the equation

$$\frac{\delta w(x, t)}{\delta t} = D(t)\frac{\delta^2 w(x, t)}{\delta x^2} - \lambda w(x, t) + \zeta(t) \tag{21}$$

with the first boundary condition

$$w(x, 0) = 0 \tag{21a}$$

and the remaining two boundary conditions analogous to (16b, c).

By the substitution

$$v = u\, \mathrm{e}^{-\lambda t} \tag{22}$$

and by the transformation

$$\tau = \int_0^t D(t)\mathrm{d}t \tag{23}$$

eqn. (20) may be reduced to

$$\frac{\delta u}{\delta \tau} = \frac{\delta^2 u}{\delta x^2} \tag{24}$$

which, under given boundaries, has the solution

$$u(x, t) = \frac{2}{l}\sum_{n=0}^{\infty} \exp\left(-\frac{n^2\pi^2}{l^2}\tau\right) \times \cos\left[\left(n + \tfrac{1}{2}\right)\pi\frac{l - x}{l}\right]\int_0^l \varphi(s)\cos\left[\left(n + \tfrac{1}{2}\right)\pi\frac{l - s}{l}\right]\mathrm{d}s \tag{25}$$

which, after backward transformation, gives

$$v(x,t) = \frac{2}{l}\,\frac{\zeta(0)}{\lambda}\exp(-\lambda t)\sum_{n=0}^{\infty}\left\{\frac{2l}{(2n + 1)\pi} - \frac{1}{\alpha^2 + \beta_n^2}\left[\beta_n - \frac{\alpha}{\sinh(\alpha l)}\right]\right\} \times \exp\left(-\frac{n^2\pi^2}{l^2}\tau\right)\cos[\beta_n(l - x)] \tag{26}$$

where

$$\alpha = \sqrt{\frac{\lambda}{D(0)}} \tag{26a}$$

and

$$\beta_n = \left(n + \frac{1}{2}\right)\frac{\pi}{l} \tag{26b}$$

In a similar way, eqn. (21) can be reduced by transformations analogous to eqns. (22) and (23) to

$$\frac{\delta z}{\delta \tau}=\frac{\delta^2 z}{\delta x^2}+\xi(\tau) \tag{27}$$

where

$$\xi(\tau)=\frac{\xi(t)}{D(t)}\mathrm{e}^{\lambda t} \tag{28}$$

The solution of eqn. (27) is

$$z(x,\tau)=\frac{2}{l}\sum_{n=0}^{\infty}\cos[\beta_n(l-x)] \times\int_0^{\tau}\xi(x)\exp\left[-\frac{\pi^2 n^2}{l^2}(\tau-x)\right]\int_0^{l}\cos[\beta_n(l-s)]\mathrm{d}s\mathrm{d}x \tag{29}$$

After algebraic manipulations, eqns. (19)–(29) give

$$c(x,t)=\mathrm{e}^{-\lambda t}\sum_{n=0}^{\infty}\cos[\beta_n(l-x)]\{b_n(t)+c_n(t)\} \tag{30}$$

where α and β_n are defined by eqn. (26a, b), respectively, and

$$b_n(t)=\frac{2}{l}\frac{\zeta(0)}{\lambda}\left\{\frac{2l}{(2n+1)\pi}-\frac{1}{\alpha^2+\beta_n^2}\left[\beta_n-\frac{\alpha}{\sinh(\alpha l)}\right]\right\} \times\exp\left[-\frac{n^2\pi^2}{l^2}\int_0^t D(\nu)\mathrm{d}\nu\right] \tag{31}$$

and

$$c_n(t)=\frac{2}{l}\exp\left[-\frac{\pi^2 n^2}{l^2}\int_0^t D(\nu)\mathrm{d}\nu\right]\int_0^t\zeta(s)\exp\left[\lambda s+\frac{\pi^2 n^2}{l^2}\int_0^t D(\nu)\mathrm{d}\nu\right]\mathrm{d}s \tag{32}$$

$\zeta(t)$ and $D(t)$ being defined in our case by eqns. (10) and (14), respectively. From eqn (30), the emanation rate ϵ_{p} due to pore diffusion follows directly

$$\epsilon_{\mathrm{p}}=N_{\mathrm{p}}D_{\mathrm{p}}\pi r_{\mathrm{p}}^2\frac{\delta c(0,t)}{\delta x}=N_{\mathrm{p}}\sqrt{\left(\frac{8\pi RT}{M}\right)}r_{\mathrm{p}}^3\mathrm{e}^{-\lambda t}\sum_{n=\theta}^{\infty}\beta_n[b_n(t)+c_n(t)] \tag{33}$$

where N_{p} is the number of uniform pores in the body. This expression can be readily generalized to the case of a distribution of pore radii: if $P(r_{\mathrm{p}})$ is some normalized distribution function, then

$$\epsilon_{\mathrm{p}}=N_{\mathrm{p}}\sqrt{\left(\frac{8\pi RT}{M}\right)}\mathrm{e}^{-\lambda t}\sum_{n=0}^{\infty}\beta_n\int_0^{\infty}P(r_{\mathrm{p}})r_{\mathrm{p}}^3\left[b_n(t,r_{\mathrm{p}})+c_n(t,r_{\mathrm{p}})\right]\mathrm{d}r_{\mathrm{p}} \tag{34}$$

Emanation rate, ϵ_R

The part of the emanation rate caused by the surface recoil depends on the outer surface of the body. Neglecting the correction due to the part of the surface which is occupied by the pores' ends (assuming it to be sufficiently small) it follows

$$\epsilon_{\mathrm{R}} = \Lambda_{\mathrm{R}} 4\pi \int_{R_{\mathrm{b}}-\rho_{\mathrm{r}}}^{R_{\mathrm{b}}} r^2 c_{\mathrm{R}}(r, t) q(r) \mathrm{d}r \tag{35}$$

where $q(r)$ is [3]

$$q(r) = \frac{2\rho_{\mathrm{r}} r - (R_{\mathrm{b}}^2 - \rho_{\mathrm{r}}^2) + r^2}{4\rho_{\mathrm{r}} r} \tag{36}$$

and $c_{\mathrm{R}}(r, t)$ is, in analogy to eqn. (3)

$$c_{\mathrm{R}}(r, t) = \frac{\Lambda_{\mathrm{T}} c_{\mathrm{T}}}{\lambda_{\mathrm{R}}} \chi(r) \tag{37}$$

where, for a homogeneous distribution of the parent isotope,

$$\chi(r) = \frac{R_{\mathrm{b}}^2 - (r - \rho_{\mathrm{R}})^2}{4r\rho_{\mathrm{R}}} \tag{37a}$$

and, for the surface impregnation

$$\chi(r) = \frac{R_{\mathrm{b}}}{r} \frac{1}{2\rho_{\mathrm{R}}} \tag{37b}$$

from the respective geometrical interpretations of probability. After algebraic manipulations, the explicit form of (35) is

$$\begin{aligned}\epsilon_{\mathrm{R}} = \frac{\pi \Lambda_{\mathrm{T}} c_{\mathrm{T}}}{4\rho_{\mathrm{R}}\rho_{\mathrm{r}}} \Bigl[& R_{\mathrm{b}}\rho_{\mathrm{r}} \Bigl\{ R_{\mathrm{b}} \bigl[\rho_{\mathrm{r}} \bigl(\tfrac{16}{3}\rho_{\mathrm{r}} - \tfrac{9}{5} R_{\mathrm{b}} + \tfrac{1}{2}\rho_{\mathrm{R}} - \tfrac{1}{2} \bigr) + \rho_{\mathrm{R}}^2 \\ & + R_{\mathrm{b}} \bigl(1 + \tfrac{3}{5} R_{\mathrm{b}}^2 + \tfrac{2}{5} R_{\mathrm{b}} + \tfrac{1}{2}\rho_{\mathrm{R}} \bigr) \bigr] \\ & - \rho_{\mathrm{r}} \bigl(3\rho_{\mathrm{r}}^2 + \tfrac{5}{2}\rho_{\mathrm{R}}\rho_{\mathrm{r}} + \rho_{\mathrm{R}}^2 + 2 \bigr) \Bigr\} \\ & + \rho_{\mathrm{r}}^3 \Bigl[\tfrac{1}{2}\rho_{\mathrm{r}} \bigl(\tfrac{7}{5}\rho_{\mathrm{r}} + 1 \bigr) + \frac{\rho_{\mathrm{R}}}{3} \Bigl(\frac{\rho_{\mathrm{r}}}{2} - \rho_{\mathrm{R}} + \tfrac{3}{2} \Bigr) - R_{\mathrm{b}} - 1 \Bigr] - R_{\mathrm{b}}^4 \rho_{\mathrm{R}} \Bigr]\end{aligned} \tag{38a}$$

for the homogeneous distribution, and

$$\epsilon_{\mathrm{R}} = \frac{\pi}{2} R_{\mathrm{b}} \Lambda_{\mathrm{T}} c_{\mathrm{T}} \frac{\rho_{\mathrm{r}}}{\rho_{\mathrm{R}}} \bigl(R_{\mathrm{b}} + \tfrac{1}{3}\rho_{\mathrm{r}} \bigr) \tag{38b}$$

for the non-homogeneous distribution, resulting from surface impregnation labelling. Under these assumptions, ϵ_{R} is clearly independent of temperature and so this part forms a constant increment of the total emanation rate.

CONCLUSIONS

From eqn. (33) the temperature-dependent part of the emanation rate under the linear heating rate κ is, for our model

$$\epsilon_{\mathrm{p}}(T) = \frac{N_{\mathrm{p}}\pi^{3/2}r_{\mathrm{po}}^{3}}{l}\exp\left[-\frac{l}{\kappa}(\lambda\Delta T + 3K_{\mathrm{P}}J_{\mathrm{T}})\right]\sum_{n=0}^{\infty}(n+\tfrac{1}{2})[b_n(T)+c_n(T)] \tag{39}$$

where

$$b_n(T) = \frac{2}{l}\frac{\zeta(0)}{\lambda}\left\{\frac{2l}{(2n+1)\pi} - \frac{1}{\alpha^2+\beta_n^2}\left[\beta_n - \frac{\alpha}{\sinh(\alpha l)}\right]\right\}\exp\left(-\frac{n^2\pi^2}{\kappa l^2}\tau\right) \tag{40}$$

and

$$c_n(T) = \frac{2}{\kappa l}\exp\left[-\frac{\pi^2 n^2}{l^2}\tau\right]\int_{T_0}^{T}\zeta(s)\exp\left[\lambda s + \frac{\pi^2 n^2}{\kappa l^2}\tau\right]\mathrm{d}s \tag{41}$$

α and β_n are defined by eqn. (26a and b), respectively. $\zeta(T)$ is defined by eqn. (10) and τ is

$$\tau = \int_{T_0}^{T}D(s)\mathrm{d}s = r_{\mathrm{p0}}\sqrt{\frac{8R}{\pi M}}\int_{T_0}^{T}s^{1/2}\exp\left[-\frac{K_{\mathrm{P}}}{\kappa}J_s\right]\mathrm{d}s \tag{42}$$

and J_{T} represents the usual temperature integral

$$J_{\mathrm{T}} = \int_{T_0}^{T}\exp(-E_{\mathrm{p}}/RT)\mathrm{d}T \tag{43}$$

The Fourier series in eqn. (39) converges absolutely so that only some terms need to be computed. Whereas good approximations for J_{T} have been found, the integral in eqn. (41) has to be obtained by some numerical method. Some features of its behaviour will be shown in the second part of this study.

Finally, we note that the inert gas diffusion in the solid in some cases cannot be neglected. The complex model of the porous solid which also includes inert gas diffusion in the solid will be treated in a paper to follow.

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