

## **THEORY OF EMANATION THERMAL ANALYSIS. V. FUNCTIONAL SCALES FOR EVALUATING THE PARAMETERS OF INERT GAS DIFFUSION IN SOLIDS**

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### **ABSTRACT**

The application of functional scales to the evaluation of diffusion parameters of inert gas diffusion in solids is shown. The linearized diffusion scales which may be applied to the evaluation of diffusion parameters and the determination of mathematical models of thermally stimulated inert gas diffusion are demonstrated.

### **INTRODUCTION**

In the previous papers of this series [1–4] the problems concerning the comparison of theoretical curves and experimental results of emanation thermal analysis have been discussed. The main difficulties are connected with the lack of simple and reliable methods for the treatment and interpretation of diffusion experiment data. The application of rapid computers is necessary for the treatment of these data because of the complexity of the mathematics of diffusion phenomena.

The task of the treatment of experimental diffusion data can be substantially simplified when using functional scales which give the possibility of linearizing non-linear dependences between the parameters investigated. There exists a possibility to construct special diffusion scale sheets by means of which the linearization of the non-linear dependences can be made directly and simply. For every technique used in emanation thermal analysis, e.g., the permeability and adsorption techniques, thermally stimulated diffusion of inert gas label [5], and other special diffusion functional scales must be designed [6,7].

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The diffusion parameters and errors of their determination can be evaluated by the least squares method using a pocket calculator. The aim of this paper is to show how the functional scales for evaluating diffusion data of various techniques of emanation thermal analysis can be constructed. The diffusion scale sheets for the treatment of thermally stimulated diffusion data are presented, taking into account various shapes of solid samples and various inert gas diffusion mechanisms.

#### PHENOMENOLOGICAL THEORY OF THE METHOD OF RADIOACTIVE INERT GAS PROBE

The method, which is based on the determination of radioactive inert gas release from a solid heated at a constant rate is generally called the method of radioactive inert gas probe. This method is considered to be one variety of emanation thermal analysis.

The determination of the stage of inert gas release has to be made before the treatment of the experimental data. The kinetic or diffusion stage of inert gas release are usually considered. The diffusion stage of the release is usually observed at temperatures when the self diffusion in the crystal lattice of solids takes place and when the inert gas is distributed in the whole volume of the sample. In this case the inert gas release can be described by the solution of Fick's laws taking into account the respective initial and limit conditions and the geometrical form of the samples investigated. The initial differential equation taking into account various geometrical shapes of the sample can be written in the form of eqn. (1)

$$\frac{\partial C}{\partial t} = D \frac{1}{r^\nu} \frac{\partial}{\partial r} \left( r^\nu \frac{\partial C}{\partial r} \right) \quad (1)$$

where  $C(r, t)$  is the concentration of inert radioactive gas,  $t$  is time,  $D$  is the inert gas diffusion coefficient,  $r$  the radial coordinate,  $\nu = 0$  for a plate, cylinder or prism with impermeable sides,  $\nu = 1$  for a cylinder or prism with impermeable bases (i.e., infinite cylinder);  $\nu = 2$  for a sphere.

Equation 1 has to be solved at the limit conditions

$$C(L, t) = 0 \quad (2a)$$

$$\partial C(0, t) / \partial x = 0 \quad (2b)$$

$$C(x, 0) = f(x) \quad (2c)$$

where  $L$  is the characteristic size of the elementary volume at the point where sample diffusion takes place, e.g., the half width of the plate or radius of the sphere or cylinder.

For homogeneous distribution of the diffusion gas in the volume of the sample  $C(x, 0) = C_0$  the solution of eqn. (1) under the limit conditions (2)

results in the time dependence of the density  $J$  of the flux of inert gas release, in eqn. (3)

$$J = \frac{2(\nu + 1)D}{L^2} \sum_{m=0}^{\infty} \exp\left(-\mu_{m,\nu}^2 \frac{D}{L^2} t\right) \quad (3)$$

where  $\mu_{m,0}$ ;  $[(2m + 1)\pi/2, \nu = 0; q_m, \nu = 1; \pi m, \nu = 2]$  and  $q_m$  are nuclei of the Bessel functions.

The existence of the temperature dependence of the diffusion coefficient causes more complicated mathematical expressions for the equation of the inert gas release flux  $J$ .

The temperature dependence of the diffusion coefficient is usually represented as

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

where  $D_0$  and  $E_d$  are the pre-exponential factor and activation energy of inert gas diffusion, respectively,  $R$  is the molar gas constant, and  $T$  is temperature (in K).

In conditions of constant heating rate the temperature increases according to the relationship

$$T = T_0 + \kappa t \quad (5)$$

where  $T_0$  is the temperature of the onset of sample heating,  $\kappa$  is heating rate (in  $\text{K s}^{-1}$ ),  $t$  is heating time (in s). Then the time dependence of the diffusion coefficient can be described by eqn. (6)

$$D(t) = D_0 \exp[-E_d/R(T_0 + \kappa t)] \quad (6)$$

The time dependence of the flux  $J$  of the inert gas release on constant heating rate of the sample can be obtained by replacement in eqn. (3) of  $D$  by  $D(t)$  (see eqn. 6) and  $Dt$  by the integral time  $\tau_i$  which is given by

$$\tau_i = \int_0^t D(\tau) d\tau = \int_{T_0}^T D(\theta) d\theta \quad (7)$$

under conditions of a linear temperature increase we can write

$$\tau_i = \frac{D_0 E_d}{\kappa R} \left[ -\frac{\exp(\tau)}{\tau} + E_i(\tau) \right] \quad \begin{aligned} \tau &= -\frac{E_d}{R(T_0 + \kappa t)} \\ \tau &= -E_d/RT_0 \end{aligned} \quad (8)$$

where  $E_i(z) = \int_{-\infty}^z \frac{\exp(\tau)}{\tau} d\tau$

Finally, in the case of a uniformly labelled sphere with radius  $r_0$ , the flux  $J$  of the inert gas from the sample is expressed by eqn. (9)

$$J = \frac{2C_0 S D_0}{r_0} \exp\left(-\frac{E_d}{RT}\right) \sum_{n=1}^{\infty} \exp\left\{-\frac{n^2 \pi^2 \tau_i}{r_0^2}\right\} \quad (9)$$

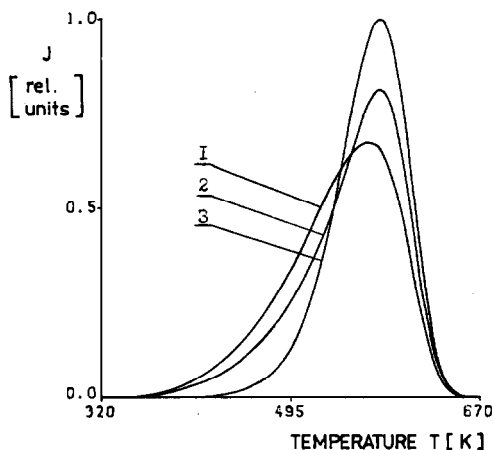


Fig. 1. Computed temperature dependences of the thermostimulated inert gas release during constant rate heating of samples of various shape, supposing various diffusion stages: curve (1) spherical sample, diffusion stage of gas release; curve (2) plate, diffusion stage of gas release; curve (3) kinetic stage of gas release. The values of  $E_d = 20000$ ,  $\ln(K_0 R / E_d) = 23$  are assumed.

where  $S$  is surface area of the sample, the constant heating rate condition being supposed.

As it follows from eqn. (9) with conditions of linearly increasing temperature, the time dependence of the inert gas flux  $J$  can be represented by an asymmetric peak-like curve (see Fig. 1).

The peak maximum temperature rises with the increase of the diffusion activation energy, radius of the grain and the sample heating rate. The decrease of the pre-exponential factor should also lead to an increase in the temperature of the peak maximum.

The kinetic stage of the inert gas release is usually observed after long diffusion times, i.e. when the majority ( $> 80\%$ ) of inert gas has been released, more precisely it is after time,  $t_x$ , equal to  $L^2/4\pi^2D$ .

However, in many cases the kinetic stage of inert gas release can be considered as the beginning of the diffusion experiment (ETA measurements). This is, e.g., the case of inert gas desorption from solid surfaces, the inert gas diffusion in highly defected solid media (e.g. meteorites and natural minerals) the inert gas diffusion from the surface layers of solids labelled by ionic bombardment or nuclear reactions, the case of solids with large surface area (e.g. zeolites) and when intense solid state processes take place during the heating of the sample (e.g. annealing of defects, phase transitions, solid state reactions, etc.).

In the kinetic stage, the inert gas release is almost independent on the initial concentration profile of the inert gas in the solid sample, the geometrical shape and size of the sample investigated; usually it takes place at

temperatures considerably lower than the volume diffusion of inert gases in the respective solids.

This behaviour can be explained by the "single-jump diffusion" model considering that for the release of inert gas atoms a small number (less than 100) of gas-atom jumps in the lattice is sufficient. Considering the kinetic stage of inert gas release, the classical diffusion equation [in eqn. (1)] can be substituted by the equation of the first order chemical reaction in eqn. (10).

$$dC/dt = -K_d C \quad (10)$$

where  $K_d = \pi^2 D/d^2$ ,  $d$  being the length of diffusion jump,  $C$  is the number of the inert gas atoms which are present in the sample at time  $t$ .

The inert gas flux  $J$  from the sample heated at a constant rate is given by eqn. (11).

$$J = C_0 K_0 \exp\left(-\frac{E_d}{RT}\right) \exp\left\{-K_0 t \exp\left(-\frac{E_d}{RT}\right)\right\} \quad (11)$$

In Fig. 1 the temperature dependences of the thermostimulated inert gas release during constant heating of spherical samples or plates are demonstrated. In calculations, the volume diffusion mechanism (curves 1 and 2) and the single jump diffusion mechanism (curve 3, Fig. 1) were considered. The main influencing factors are the geometrical shape of the grains and the diffusion mechanism of the inert gas. Supposing the same parameters of the inert gas diffusion, the size of the samples and the volume diffusion mechanism of inert gas, curve 1 in Fig. 1 results for spherical samples, with the maximum at a lower temperature than in the case of plates or samples of other shapes (Fig. 1, curve 2). When single-jump diffusion is considered, the inert gas release curves are more symmetric and the peak is sharper (Fig. 1, curve 3) than in the curves of the volume diffusion mechanism, and are independent of the shape of the sample.

#### CALCULATION AND PLOTTING OF FUNCTIONAL SCALES

The example of the functional scale construction for the case of kinetic stage inert gas release will be given later. Equation (11) can be written in the following form

$$\begin{aligned} F(U) = F\left(\frac{E_d}{RT} - \frac{E_d}{RT_m}\right) &= J(T)/J(T_m) = \exp\left[-\left(\frac{E_d}{RT} - \frac{E_d}{RT_m}\right)\right] \\ &\times \exp\left\{-\frac{K_0}{\kappa} \left[\frac{RT}{E_d} \exp\left(-\frac{E_d}{RT}\right) - \frac{RT_m}{E_d}\right]\right\} \\ &\times \exp\left(-\frac{E_d}{RT_m}\right) - E_i\left(-\frac{E_d}{RT}\right) + E_i\left(-\frac{E_d}{RT_m}\right) \Bigg\} \quad (12) \end{aligned}$$

TABLE 1

Functional scale for linearization of the curves of thermostimulated inert gas release in kinetic stage

F(U)	U (Increasing)	U (Decreasing)	F(U)	U (Increasing)	U (Decreasing)
0.02	4.8065	-1.7861	0.52	1.3513	-0.9029
0.04	4.1082	-1.6693	0.54	1.3024	-0.8807
0.06	3.6972	-1.5915	0.56	1.2545	-0.8586
0.08	3.4036	-1.5307	0.58	1.2074	-0.8363
0.10	3.1744	-1.4801	0.60	1.1612	-0.8139
0.12	2.9858	-1.4357	0.62	1.1155	-0.7912
0.14	2.8253	-1.3959	0.64	1.0704	-0.7683
0.16	2.6851	-1.3597	0.66	1.0257	-0.7451
0.18	2.5605	-1.3258	0.68	0.9814	-0.7216
0.20	2.4481	-1.2943	0.70	0.9373	-0.6975
0.22	2.3456	-1.2643	0.72	0.8932	-0.6730
0.24	2.2513	-1.2357	0.74	0.8491	-0.6478
0.26	2.1637	-1.2083	0.76	0.8048	-0.6219
0.28	2.0818	-1.1819	0.78	0.7602	-0.5951
0.30	2.0048	-1.1564	0.80	0.7151	-0.5673
0.32	1.9321	-1.1315	0.82	0.6692	-0.5383
0.34	1.8631	-1.1072	0.84	0.6222	-0.5079
0.36	1.7973	-1.0834	0.86	0.5740	-0.4756
0.38	1.7344	-1.0600	0.88	0.5238	-0.4410
0.40	1.6740	-1.0369	0.90	0.4711	-0.4037
0.42	1.6159	-1.0142	0.92	0.4148	-0.3621
0.44	1.5598	-0.9917	0.94	0.3533	-0.3150
0.46	1.5054	-0.9693	0.96	0.2829	-0.2589
0.48	1.4527	-0.9471	0.98	0.1952	-0.1851
0.50	1.4014	-0.9250	1.00	0.0000	0.0000

where  $T_m$  is the temperature of the peak maximum.

$$\ln K_0/\kappa - \ln E_d/R + 2 \ln T_m - E_d/RT_m = 0 \quad (13)$$

In order to prepare the diffusion scale sheets the values of  $F(U)$  are calculated, and by subsequent dividing the  $F(U)$  function into several intervals, the  $U$ -values are found which correspond to the  $F(U)$  values. The calculated values for the case of the kinetic stage of gas release are given in Table 1; for the examples of volume diffusion from plate and spherical samples, see Tables 2 and 3, respectively.

The functional scale is written directly on the ordinate axis: on the right of the axis the values of  $U$  in the normal scale are given, on the left the corresponding values of  $F(U)$  in the functional scale are presented; the values of  $1/T$  ( $K^{-1}$ ) are given on the abscissae.

The experimental results of thermostimulated inert gas release represent,

TABLE 2

Functional scale for linearization of the curves of thermostimulated inert gas release from plate

F(U)	U (Increasing)	U (Decreasing)	F(U)	U (Increasing)	U (Decreasing)
0.02	8.4556	-1.7902	0.52	1.7647	-0.9066
0.04	7.3566	-1.6733	0.54	1.6808	-0.8845
0.06	6.5105	-1.5955	0.56	1.5999	-0.8623
0.08	5.8842	-1.5347	0.58	1.5218	-0.8400
0.10	5.3969	-1.4841	0.60	1.4463	-0.8175
0.12	4.9982	-1.4397	0.62	1.3733	-0.7949
0.14	4.6605	-1.3999	0.64	1.3025	-0.7720
0.16	4.3676	-1.3637	0.66	1.2338	-0.7487
0.18	4.1089	-1.3298	0.68	1.1671	-0.7251
0.20	3.8773	-1.2982	0.70	1.1022	-0.7011
0.22	3.6676	-1.2683	0.72	1.0390	-0.6765
0.24	3.4759	-1.2397	0.74	0.9773	-0.6513
0.26	3.2995	-1.2122	0.76	0.9168	-0.6253
0.28	3.1359	-1.1859	0.78	0.8574	-0.5985
0.30	2.9836	-1.1603	0.80	0.7987	-0.5706
0.32	2.8409	-1.1354	0.82	0.7406	-0.5416
0.34	2.7069	-1.1110	0.84	0.6826	-0.5111
0.36	2.5805	-1.0872	0.86	0.6243	-0.4787
0.38	2.4608	-1.0638	0.88	0.5652	-0.4440
0.40	2.3471	-1.0408	0.90	0.5044	-0.4066
0.42	2.2389	-1.0180	0.92	0.4409	-0.3648
0.44	2.1357	-0.9955	0.94	0.3730	-0.3175
0.46	2.0371	-0.9731	0.96	0.2968	-0.2610
0.48	1.9426	-0.9509	0.98	0.2039	-0.1865
0.50	1.8519	-0.9287	1.00	0.0000	0.0000

in the normal scale, the peak-shaped curves, which are usually normalized with respect to the height of the maximum; in the linearized functional scale these results represent the dependence of  $Y(T)/Y(T_m) = F(U)$  vs.  $1/T$ . Every point in the curve is determined by two coordinates:  $1/T$  and  $U$ ; the constructed dependence between  $U$  and  $1/T$  can be described by the linear relationship in eqn. (14)

$$U = \frac{E_d}{RT} - \frac{E_d}{RT_m} = \frac{E_d}{RT} - \ln \frac{K_0 RT_m^2}{E_d \kappa} = \frac{E_d}{RT} + A \quad (14)$$

where  $A$  is the part of the ordinate axis which can be used for the calculation of the pre-exponential factor of diffusion.

$$\ln K_0 = - \left( \frac{A}{a} + \ln \frac{RT_m^2 a^2}{\kappa E_d} \right) \quad (15)$$

TABLE 3

Functional scale for linearization of the curves of thermostimulated inert gas release from spherical sample

$F(U)$	$U$ (Increasing)	$U$ (Decreasing)	$F(U)$	$U$ (Increasing)	$U$ (Decreasing)
0.02	8.8621	-2.1008	0.52	2.5030	-1.1761
0.04	7.9960	-1.9818	0.54	2.4039	-1.1517
0.06	7.3701	-1.9019	0.56	2.3072	-1.1271
0.08	6.8234	-1.8396	0.58	2.2127	-1.1022
0.10	6.3456	-1.7873	0.60	2.1200	-1.0771
0.12	5.9423	-1.7415	0.62	2.0291	-1.0515
0.14	5.5985	-1.7003	0.64	1.9397	-1.0255
0.16	5.2989	-1.6626	0.66	1.8515	-0.9990
0.18	5.0331	-1.6275	0.68	1.7644	-0.9719
0.20	4.7938	-1.5945	0.70	1.6781	-0.9440
0.22	4.5761	-1.5630	0.72	1.5925	-0.9153
0.24	4.3760	-1.5332	0.74	1.5073	-0.8857
0.26	4.1907	-1.5044	0.76	1.4223	-0.8548
0.28	4.0179	-1.4765	0.78	1.3371	-0.8226
0.30	3.8560	-1.4494	0.80	1.2516	-0.7889
0.32	3.7033	-1.4230	0.82	1.1653	-0.7533
0.34	3.5588	-1.3972	0.84	1.0777	-0.7154
0.36	3.4215	-1.3718	0.86	0.9883	-0.6747
0.38	3.2906	-1.3467	0.88	0.8964	-0.6306
0.40	3.1653	-1.3220	0.90	0.8008	-0.5815
0.42	3.0450	-1.2975	0.92	0.6999	-0.5270
0.44	2.9292	-1.2731	0.94	0.5910	-0.4632
0.46	2.8176	-1.2489	0.96	0.4688	-0.3854
0.48	2.7095	-1.2247	0.98	0.3195	-0.2799
0.50	2.6048	-1.2004	1.00	0.0000	0.0000

where  $a$  is the coefficient of the geometry of the sample ( $a = 1$  for single jump diffusion,  $a = 1.0029$  for a plate-shaped sample,  $a = 1.01907$  for a sphere).

The activation energy of diffusion can be expressed as follows:

$$E_d = R \operatorname{tg} \alpha \quad (16)$$

The experimental curves of the thermally stimulated diffusion in the normal scale and in the functional scale are represented in Figs. 2 and 3, respectively. In this way the initial peak-shape temperature dependence of the inert gas release is transformed to a linear dependence; the maximum temperature of the peak  $T_m$  corresponds to  $U = 0$ , the low temperature-increasing part of the peak ( $T < T_m$ ) is reflected by values  $U > 0$ , the high temperature-decreasing part of the peak ( $T > T_m$ ) is reflected by values  $U < 0$ .



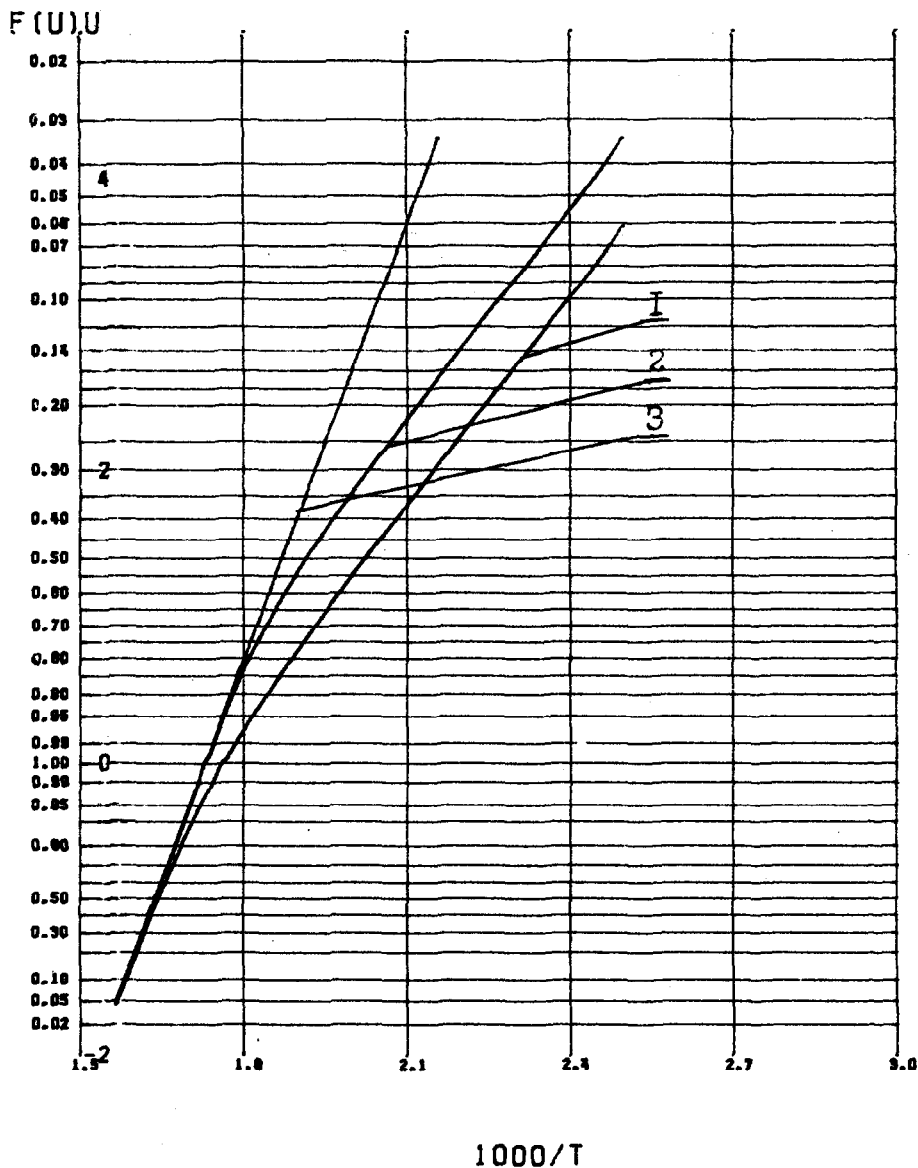


Fig. 2. The linearized temperature dependences of the thermostimulated inert gas release during constant rate heating of the spherical and plate samples, considering different stages of inert gas release. The notation of the curves is the same as in Fig. 1.

There are several advantages of this simple method of treatment of diffusion experimental data. The linearized dependences of inert gas release enabled us to calculate easily the diffusion parameters using all points of the ETA curve. The suitability of the diffusion model used for the construction of the inert gas release curve can be estimated according to the correlation

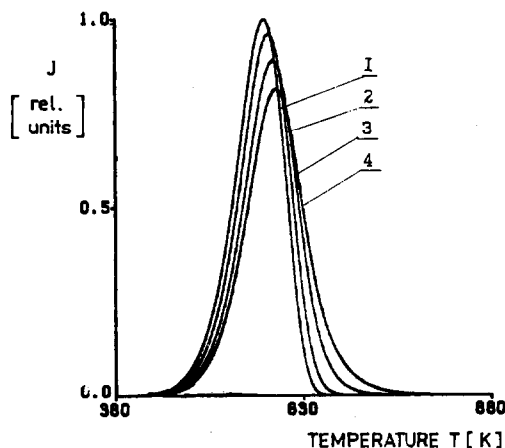


Fig. 3. The influence of the inertia of the apparatus on the temperature dependences of thermostimulated inert gas release: (various values of parameter  $Z$  being considered): curve (1)  $Z \rightarrow \infty$  (idealized case for the measuring chamber with the volume  $V \rightarrow 0$ ); curve (2)  $Z = 0.5$ ; curve (3)  $Z = 0.25$ ; curve (4)  $Z = 0.167$ .

coefficient value. The most suitable diffusion model is the one that the corresponding correlation coefficient is close to unity.

#### APPLICATION OF THE FUNCTIONAL SCALES IN ANALYSIS OF ETA CURVES INFLUENCED BY VARIOUS FACTORS

The real ETA curves demonstrating the temperature dependence of the inert gas release by thermal desorption or diffusion are influenced by the shape of solid grains and by the inertia of the apparatus. Moreover, the curves of the thermostimulated inert gas release are dependent on the diffusion mechanism, i.e., for interaction between inert gas atoms with defects of the lattice, multichannel diffusion and solid state reactions. Consequently, in practice the ETA curves do not correspond perfectly to the idealised diffusion cases discussed above. Sometimes the real curves of inert gas release cannot be fully linearized by using the functional scales. Nevertheless, the application of functional scales to the evaluation of the real curves enabled us, even in these cases, to assess the diffusion behaviour of the solid: the deviation from the ideal diffusion case was evaluated and the diffusion parameters were determined from the linear part of the dependence of the functional scale.

#### *Geometrical shape of solid grains*

The shape of the grains of the solid powders investigated is usually not uniform and well defined. Moreover, the characteristic size of the elemen-

tary volume  $L$  may not correspond to the grain radius; the dispersed solid samples contain aggregates of grains the shape and size of which determine the real diffusion time. It is known, that in case of powders of large surface area and expanded surface relief, the diffusion does not depend on the size and shape of the sample and is determined by the parameters of the crystal lattice only. Similarly, parameters of inert gas diffusion in the samples prepared as pellets from fine particles were determined. We have observed that in the case of well-pressed, dense pellets the inert gas release from the pellet can be described by the diffusion equations derived for plates, in the case of poorly pressed pellets, the inert gas release can be described by the equation derived for a sphere.

The determination of the grain shape (which is then used in the diffusion model) of the sample can be made by comparing the experimental ETA curve with the ETA curve calculated for various shapes of sample, in the functional scales. The best-suited sample shape results in the corresponding correlation coefficient closest to unity.

The influence of the shape of the sample on the curve of thermostimulated inert gas release has been discussed in Fig. 1. The respective curves, corresponding to the shape of plate and sphere are replotted in Fig. 2, using functional scales. It is evident that the functional scale for the single jump diffusion model in Fig. 2 should be considered as the basic scale for comparing various diffusion models and shapes. The change of the geometric shape of the sample is reflected in Fig. 2 by the deviation from the linear dependence in the low temperature range. In the high temperature range the correct values of the activation energy of inert gas diffusion can be determined from the linear part of the dependence.

### *The inertia of the apparatus*

In our previous publications [5,8] a detailed analysis of the influence of inertia of the apparatus on the ETA curve was made. The distortion of the curve of thermostimulated inert gas release in the measuring chamber is expressed by eqn. (17).

$$N(t) = N_0 \exp[-z(t)] + \int_0^t \exp[-z(t-\tau)] F(\tau) d\tau \quad (17)$$

where  $N(t)$  is the number of inert gas atoms in the measuring chamber at time  $t$ ,  $F(t)$  is the velocity of inert gas input into the measuring chamber [depending on the geometrical shape of the sample and determined from eqn. (3)],  $Z$  is the total velocity of the inert gas output from the measuring chamber ( $z = \delta/V$ , being the flow rate of the carrier gas),  $V$  is the volume of the measuring chamber.

The temperature dependences of the thermostimulated inert gas release calculated from eqn. (11) for the kinetic stage of the gas release, taking into

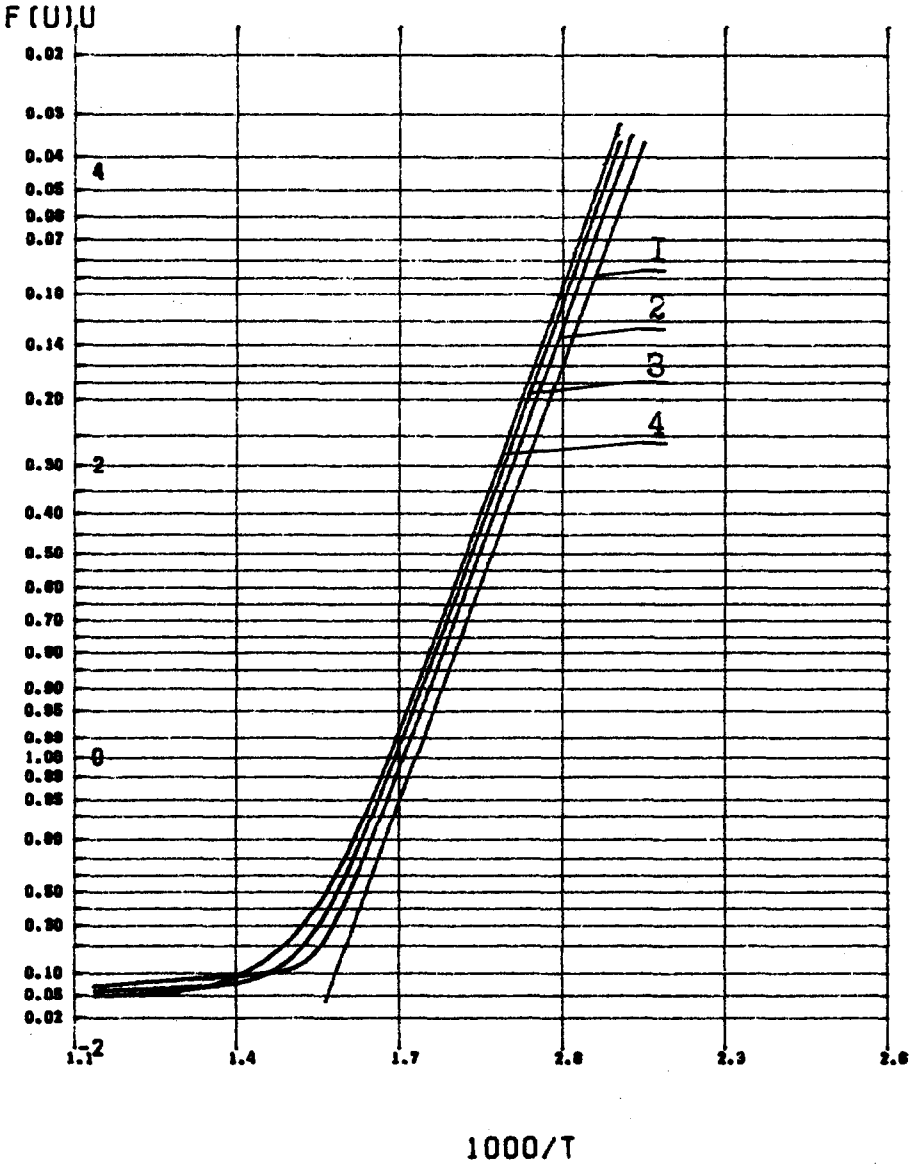


Fig. 4. The linearized temperature dependences of thermostimulated inert gas release taking into account the influence of the inertia of the apparatus (for notation of the curves see Fig. 3).

account the distorting effect of the inertia of the apparatus, are shown in Fig. 3.

The thermal dependences of Fig. 3 plotted in the functional scale are shown in Fig. 4. It is obvious that the main distorting effect of the apparatus inertia is pronounced on the high temperature part of the peak. The lower

the value of  $Z$ , the more distorted are the curves. As follows from Fig. 3, there are sufficient linear parts of the curves to be used for calculating activation energy of diffusion. The inertia of the apparatus, however, results in incorrect values of the pre-exponential factors of the inert gas diffusion.

### *The order of the thermodesorption reaction*

The kinetics of the inert gas release can be affected in some cases by mutual interactions of inert gas atoms or by the inert gas interactions with the defects (irregularities, impurities) of the solid structure. In this case the differential diffusion equation is expressed as follows:

$$J(t) = -\frac{dC}{dt} = K_0 C^n \exp\{-E_d/R(T_0 + \kappa t)\} \quad (18)$$

where  $n$  is the formal order of reaction. Formation of gas associates is characterized by  $n=2$ , i.e. by the second order equation of chemical reaction. In this case the peak width is not greater than that for  $n=1$ , and the temperature of the peak  $T_m$  and its height depend on the initial inert gas concentration  $C_0$  in the sample. It is to be noted that the high probability of the inert gas trapping in the solid structure, characterized by  $n=2$  in eqn. (18), has to be reflected by the volume distribution functions of the inert gas.

Figure 5 shows the temperature dependences of the inert gas release curves as influenced by various values of  $n$ ; in Fig. 6 the same dependences plotted on a linearized scale are shown. As can be seen from Fig. 5, the order  $n$  of the inert gas trapping reaction can be estimated from the shape of

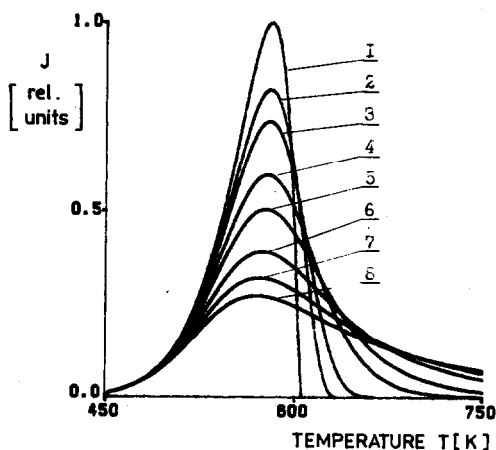


Fig. 5. Temperature dependences of the thermostimulated inert gas release influenced by the inert gas trapping in the lattice of the solid. The following orders  $n$  of reaction between inert gas and lattice traps are considered, curves 1–8, respectively:  $n = 0.5, 0.8, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0$ .

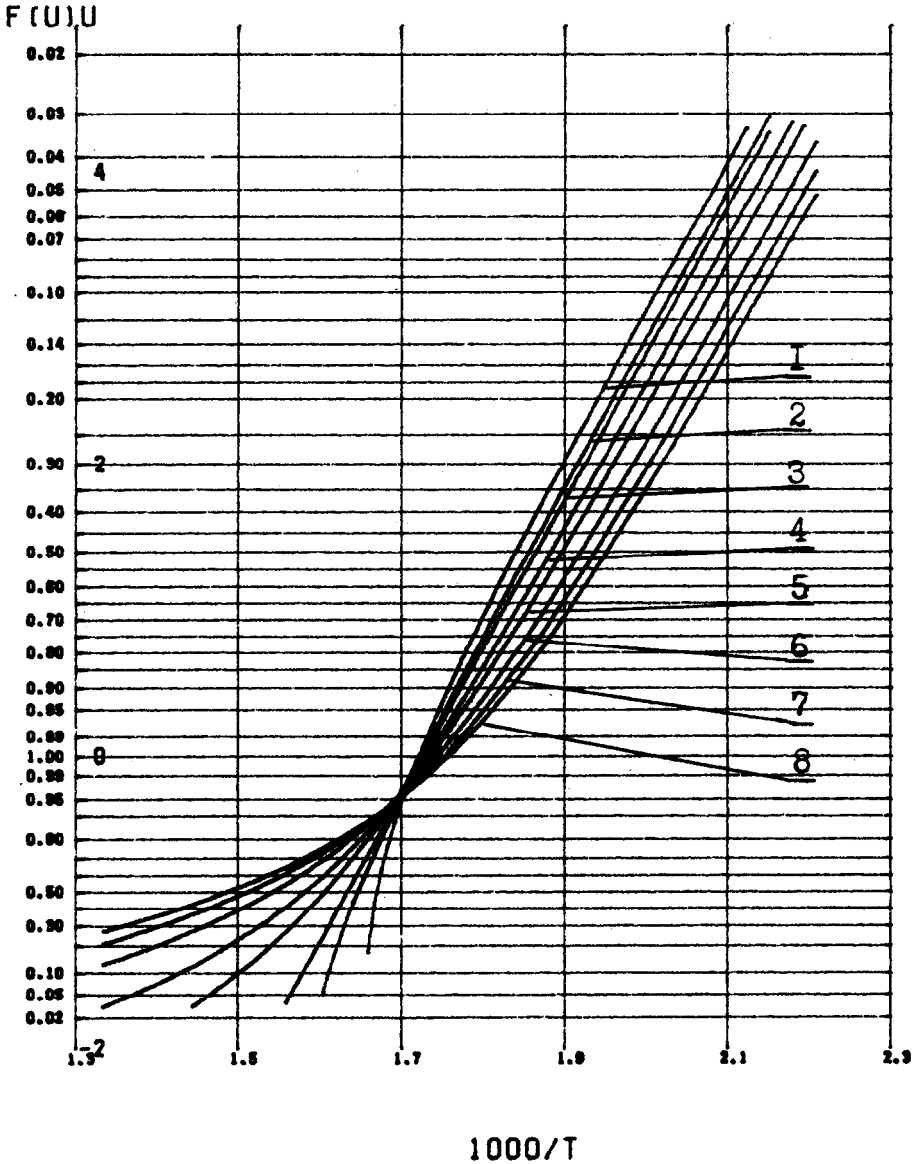


Fig. 6. The linearized plots of the temperature dependences of thermostimulated inert gas release supposing various orders  $n$  of the trapping reaction between the inert gas and the lattice traps. For notation of the curves see Fig. 5.

the inert gas release curve. In Fig. 6 the linearized inert gas release curves are shifted for  $n > 1$  and  $n < 1$  with respect to  $n = 1$ . In the low temperature range, shift to the left is observed for  $n < 1$  and shift to the right for  $n > 1$ , the slope of the linearized curves being unchanged. In the high temperature range, inverse shift in the curves is observed with respect to the curve

corresponding to  $n = 1$ , the dependences excepted that for  $n = 1$  became non-linear.

It should be pointed out that in the low temperature range the slope of the linearized curves in Fig. 6 does not depend on  $n$  and the correct value of diffusion activation energy can be evaluated for the linear parts of the curves.

#### FUNCTIONAL SCALE FOR RELEASE OF INERT GASES FROM SOLIDS LABELLED BY THEIR PARENT NUCLIDES

In this case of labelling solids by parent nuclides of inert radioactive gases, the inert gases are formed by spontaneous radioactive decay of the parent, e.g.,  $^{228}\text{Th} \xrightarrow{\alpha} ^{224}\text{Ra} \xrightarrow{\alpha} ^{220}\text{Rn}$ . The inert gas diffusion in the presence of the inert gas source is described by eqn. (19)

$$\frac{\partial C_2}{\partial t} = D \frac{\partial^2 C_2}{\partial x^2} + \lambda_1 C_1 - \lambda_2 C_2 \quad (19)$$

where  $\lambda_1$  and  $\lambda_2$  are the decay constants of the parent isotope and the inert gas, respectively,  $C_1$  and  $C_2$  are the concentrations of the parent and inert gas, i.e. Ra and Rn, respectively.

In the steady state of diffusion, the normalized diffusion flux (emanating power  $\epsilon$ ) is expressed by eqn. (20):

$$\epsilon = 3y[(1/\text{th}(1/y)) - y] \quad (20)$$

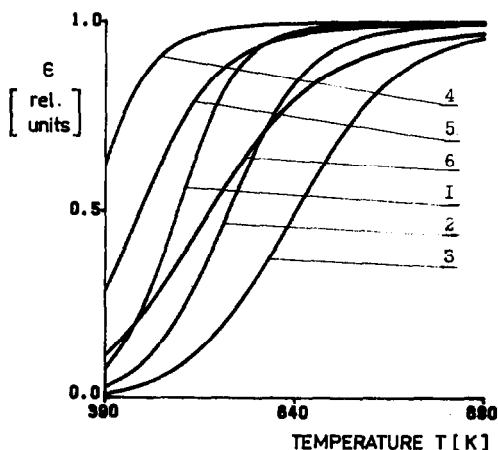


Fig. 7. Computed temperature dependences of emanating power during constant heating rate of plate sample labelled by the parent isotope of radon  $^{220}\text{Rn}$ . The following values of  $E_d$  ( $\text{kcal mol}^{-1}$ ) and  $\ln D_0/L^2\lambda_2$  respectively, were considered in the calculations of curves 1-6: (1) 16 and 9; (2) 16 and 7; (3) 16 and 5; (4) 10 and 6; (5) 10 and 4; (6) 10 and 2.

TABLE 4

Functional scale for release of inert gases from solids labelled by their parent nuclides

$F(U)$	$U$ (Increasing)	$U$ (Decreasing)	$F(U)$	$U$ (Increasing)	$U$ (Decreasing)
0.01	15.7670	0.34	8.4418	0.67	6.5722
0.02	14.3741	0.35	8.3734	0.68	6.5177
0.03	13.5564	0.36	8.3064	0.69	6.4627
0.04	12.9740	0.37	8.2407	0.70	6.4071
0.05	12.5208	0.38	8.1763	0.71	6.3508
0.06	12.1491	0.39	8.1131	0.72	6.2937
0.07	11.8335	0.40	8.0510	0.73	6.2357
0.08	11.5593	0.41	7.9899	0.74	6.1766
0.09	11.3165	0.42	7.9298	0.75	6.1165
0.10	11.0983	0.43	7.8705	0.76	6.0552
0.11	10.9002	0.44	7.8121	0.77	5.9924
0.12	10.7187	0.45	7.7544	0.78	5.9281
0.13	10.5510	0.46	7.6974	0.79	5.8620
0.14	10.3951	0.47	7.6411	0.80	5.7940
0.15	10.2492	0.48	7.5853	0.81	5.7238
0.16	10.1122	0.49	7.5301	0.82	5.6512
0.17	9.9830	0.50	7.4754	0.83	5.5757
0.18	9.8605	0.51	7.4211	0.84	5.4971
0.19	9.7442	0.52	7.3672	0.85	5.4148
0.20	9.6332	0.53	7.3137	0.86	5.3283
0.21	9.5272	0.54	7.2604	0.87	5.2370
0.22	9.4256	0.55	7.2074	0.88	5.1399
0.23	9.3280	0.56	7.1546	0.89	5.0362
0.24	9.2341	0.57	7.1019	0.90	4.9244
0.25	9.1435	0.58	7.0493	0.91	4.8028
0.26	9.0560	0.59	6.9968	0.92	4.6690
0.27	8.9714	0.60	6.9443	0.93	4.5197
0.28	8.8893	0.61	6.8917	0.94	4.3499
0.29	8.8096	0.62	6.8391	0.95	4.1522
0.30	8.7322	0.63	6.7862	0.96	3.9139
0.31	8.6568	0.64	6.7332	0.97	3.6113
0.32	8.5834	0.65	6.6799	0.98	3.1912
0.33	8.5118	0.66	6.6263	0.99	2.4833

where  $y = (1/L)(D/\lambda_2)^{1/2}$  and the temperature dependence of  $D$  is determined by eqn. (4). The temperature dependences of emanating power for various values of activation energy of diffusion and pre-exponential factors are demonstrated in Fig. 7. In Fig. 8 these temperature dependences are shown in a linearized scale (for the calculation of the functional scale see Table 4).

It is obvious that from the linear dependences in Fig. 8 the activation



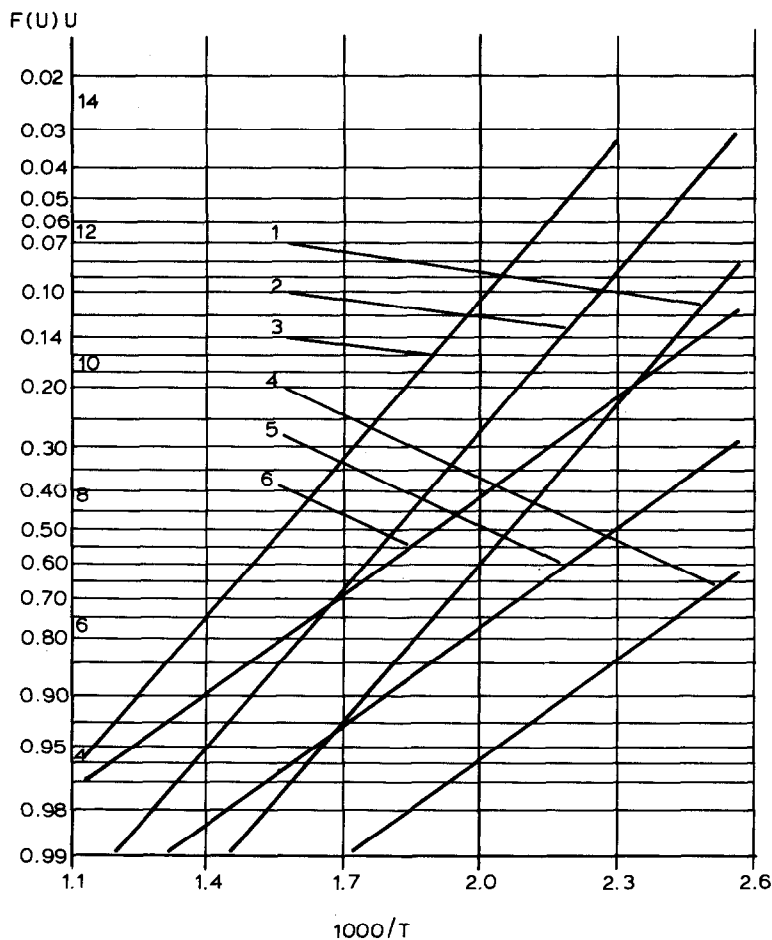


Fig. 8. The linearized temperature dependences of emanating power during constant heating rate of plate samples labelled by the parent isotope of radon. For notation of curves 1–6 see Fig. 7.

energy of diffusion and pre-exponential factor of diffusion can be easily evaluated.

## CONCLUSION

The examples of application of the functional scales to the evaluation of diffusion parameters from the ETA curves presented in this paper promise a bright perspective to this method. The tasks which may be solved only by rapid computers [3], such as choice of the appropriate diffusion model, analysis of the diffusion model and determination of inert gas diffusion parameters and their errors can be easily solved when applying the functional scales using only a pocket calculator.

## REFERENCES

- 1 J. Kříž and V. Balek, *Thermochim. Acta*, 71 (1983) 175.
- 2 J. Kříž and V. Balek, *Thermochim. Acta*, 71 (1983) 175.
- 3 V. Balek and J. Kříž, *Thermochim. Acta*, 78 (1984) 377.
- 4 V. Balek, *Thermochim. Acta*, 22 (1978) 1.
- 5 I.N. Beckman, A.A. Schviryaev and V. Balek, *Thermochim. Acta*, 104 (1986) 255.
- 6 A.A. Schviryaev and I.N. Beckman, *Vestn. MGU, Ser. 2, Khimia*, 22 (1981) 517.
- 7 I.N. Beckman, *Radiochimia*, 25 (1983) 252.
- 8 I.N. Beckman and A.A. Schviryaev, *Vestn. MGU, Ser. 2, Khimia*, 22 (1981) 467.