METHOD RADIOACTIVE INERT GAS DIFFUSION PROBE IN THE STUDY OF SOLID STATE PROCESSES

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The paper dedicated to Prof. A.Kettrup at the occasion of his 60th birthday

ABSTRACT

The principles of thermostimulated radioactive inert gas release analysis (TRIGRA), based on the measurement of noble gas migration in solids, are given. The potential and various applications of this method are demonstrated, e.g. the determination of inert gas mobility in oxides, diagnostics of materials, the investigation solid-state processes in hydroxides and oxides (generation and annealing of defects, dehydration of hydroxides, solid-state transformation, etc.).

INTRODUCTION

The method radioactive inert gas diffusion probe (RIGDiP-method) is based on the measurement of radioactive noble gases released from solids. The two versions of the RIGDiP method are available: thermostimulated radioactive inert gas release analysis (TRIGRA) and emanation thermal analysis (ETA). The atoms of radioactive nuclides of rare gases (e.g. $24^{\wedge\wedge}39^\wedge$, 85Kr, $133x^\wedge$ $220Rn^\wedge$ 222Rn) are used as trace indicators or a microprobe of the defect state of the solids and its changes [1]. The inert gas atoms do not react with the solid matrix and their release is controlled primarily by diffusion. A high sensitivity of the method to fine changes in the solid materials, phase and structure changes was observed. From the comparison of the thermoanalytical method results with the results of TRIGRA and ETA is follows that the RIGDP brings about new insight into microstructure changes taking place in the samples as a result of the solid state reaction.

In this paper the applications of the RIGDP to the diagnostics of materials are given. Implementations to solid-state processes are illustrated on the investigation solid-state processes in hydroxides and oxides.

EXPERIMENTAL ARRANGEMENT

The main problem of RIGDiP is the calculation of the parameters of the solid phase reactions from date on the kinetics of the radioactive gas probe release under conditions of heating. One of the first stages in the development of quantitative TRIGRA and ETA methods is the construction of apparatus that makes it possible to compare the kinetics of radioactive inept gas probe release with the kinetics of the solid-phase processes. In particular, in the study of topochemical reactions that are accompanied by the evolution of gaseous products it is desirable to compare the release of inert gas probe with the evolution of products of the solid-phase reaction.

The equipment should make it possible to carry out rapid-response measurements on fast processes. In the case of the formation of a mixture of gaseous reaction products, the apparatus should make it possible to record continuously each reaction product separately. The tradition analysis methods such as TGA and gas chromatographic methods do not satisfy these requirements. In the case of TGA this is connected with the impossibility of the quantitative analysis of the curve when there are several substances in the gaseous decomposition products. In the case of gas chromatographic methods, the procedure for taking samples is incompatible with the need for rapid response.

In the our work have been developed a combined apparatus, which makes it possible to carry out a continuous analysis of the radioactive inert gases release and gaseous products of a reaction in the solid phase under conditions of rapid change in their concentrations. For this purpose continuous automatic recording of the concentration of each component separately was achieved. The equipment of two types was designed: the high vacuum apparatus with radiometric and mass-spectrometric detectors and the flow apparatus with radiometric detector of the spectroscopic type.

A experimental flexible equipment has been designed for study of kinetics of both stable and radioactive gases diffusion and dissolution in various-kind materials under thermal, radiation, mechanical and chemical effects on the materials.
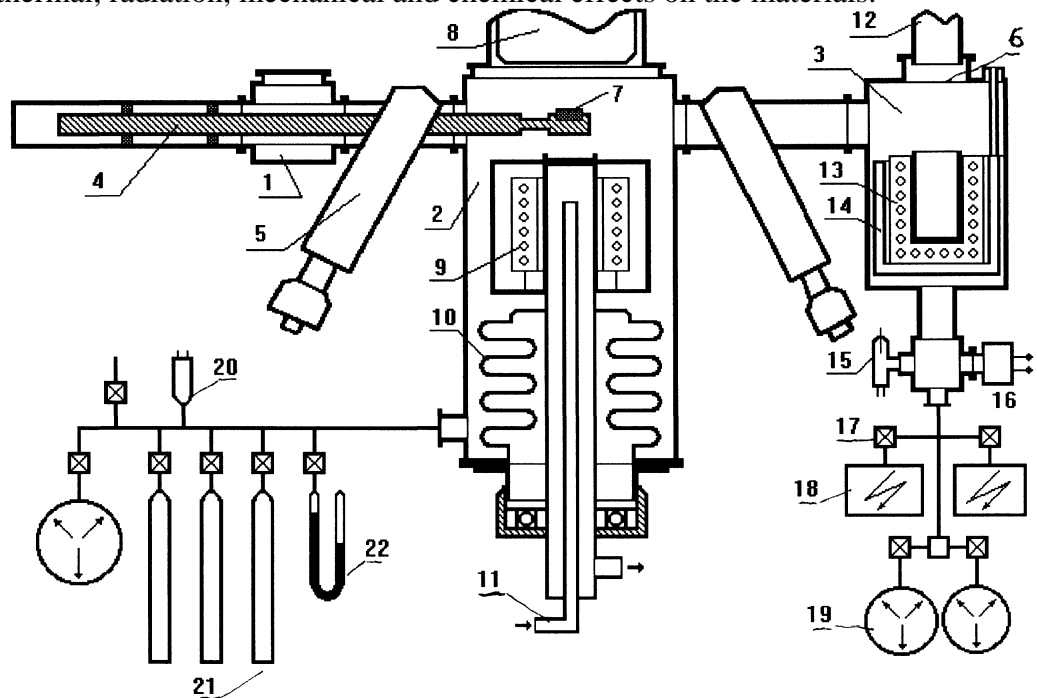

Fig.1. Block diagram of an vacuum experiment plant for introduction inert gases in solids and studying the of radioactive and stable gas release 1- chamber for load of specimens, 2- saturation chamber, 3- outgassing chamber, 4- manipulator, 5-free-flow valve, 6-beryllium window, 7-studied sample, 8-ion gun and device for glow discharge, 9- device for sample heating and temperature control (temperature range from -100 to +1000°C), 10-silfon, 11-device for introducing liquid nitrogen vapour. 12—gamma—radiation source or device for sample deformation, 13-device for sample heating and temperature control (temperature range from -150 to +1500°C), 14-vessel with liquid nitrogen, 15—mass-spectrometer, 16—a—particles detector, 17—vacuum valve, 18— sputter ion pump, 19-adsorption pump, 20-high vacuum gauge, 21-noble gases cylinders, 22— Hg— gauge

The equipment for performance of the experiment (Fig.l) consist of
- chamber for load of specimens
- saturation chamber (cell for noble gas introduction in solid)
- ion gun and device for glow discharge
- outgassing chamber (reaction cell)
- manipulator (specimen holder is seated on a transfer device than serves for transported the sample from sample cell into the saturation chamber and subsequently into outgassing chamber)
- two flow valves
- device for sample heating and temperature control (temperature range from -100to+1500°C).

- oil-free evacuation system comprising two independent vacuum units and providing ultrahigh vacuum in every section of equipment.

- ionising radiation detector and radiation sensitive instrument set for studying the of radioactive gas release (For gas activity measurement a scintillation counter was be used).

- mass spectrometer (Omegatron) for recording the stable inert gas release

- gas and gas mixture purification and bleeding-in system

- beryllium windows for the introduction of intensive ionising radiation into the diffusion chamber to study reaction and diffusion processes in the radiation field

- devices for the deformation of the sample in the course of the diffusion processes

- IBM computer-based automatic control system providing the control of all experiments, the processing and interpretation of the results.

The vacuum experiment complex makes it possible:

- to measure the kinetics of the diffusion of stable or radioactive gases or gas mixtures in or from various materials (metals, ceramic, glass, polymers), using different diffusion methods (sorption, desorption and thermodesorption, etc.)

-to study the diffusion under thermal, chemical, radiation and mechanical effects on the sample

- to study the material surface state by the diffusion inert gas probe method (thermodesorption spectroscopy or emanation thermoanalysis)

- to study of solid state reaction and solid transformation by the thermostimulated gas evolution method

- to study the pattern of the diffusing radioactive gas distribution over the surface and in the volume of the material by the authoradiography method.
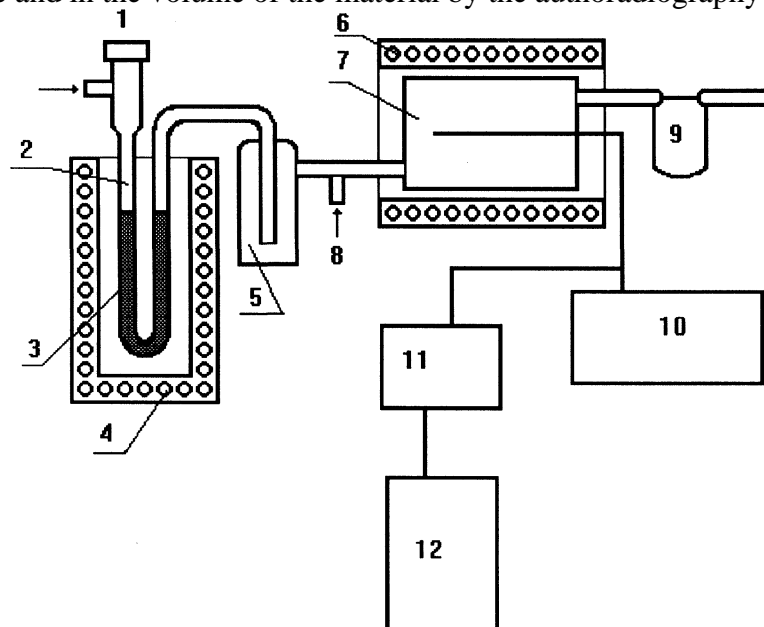

Fig. 2. Block diagram of ETA apparatus for express analysis of mixtures of radioactive gases and vapours.

1-device for introducting gas mixture, 2-column, 3-packing, 4-external heater of column, 5-trap for unreacted vapours, 6-heater of sample, 7-proportional flow counter of radiation, 8-system for introducing quenching additive, 9-rheometer, 10-high-voltage stabilizer, 11-radiation ratemeter, 12-multipoint electronic potentiometer

The operation of the experimental arrangement is a follows: the sample is mounted in a holder and than with the help of a manipulator it transferred in the cell for gas introduction. Radioactive gas is inserted into the material. The sample is frizzed by of liquid nitrogen vapour and transported in the high vacuum cell for gas evolution. The

specimen is dumped into the reaction vessel heated by an electrical furnace, the temperature program of which is controlled by a temperature control unit. The temperature is measured by thermocouples placed in the sample holder. In the course of the experiment the radioactive inert gas release and evolution of the gaseous products of solid state reaction recorded by radioactive ray detector and mass-spectrometer, respectively. IBM computer used for collection of experimental date. If required, the sample may undergo deformation and be exposed a X-radiation.

The difficulties of continuous automatic recording of each component of gas mixture separately can be overcome by using radioactive tracers. With this aim, the "two tracers" method have been successfully applied. In the chemical compound is being investigation a functional group which in course of thermodegradation processes' forms of gaseous products was chosen. In functional group the stable isotope was replaced by radionuclides of the same element. In the labelled sample the radioactive inert gas probe was introduced.

The flow apparatus provided for simultaneous performance of different physicochemical analysis methods, i.e., DTA, TG/DTG, and DL under the same thermal conditions, as well as automatic recording of radioactive inert gas probe and radioactive gaseous products of thermal decomposition. The above objective has been achieved in a flow system by means of spectroscopic analysis of the radiation energies of the radioactive components of the gas mixture.

A combined apparatus has been developed, which makes it possible to carry out a continuous analysis of the radioactive gas mixture under conditions of rapid change in their concentrations [2]. A block diagram of the apparatus is shown in Fig.2. The apparatus consists of a system for introducing the gas mixture (1), a system for rapid-response conversion (where necessary) of the components of the gas mixture into a convenient form for registration (the system consisted of a column (2) with a packing (3) and an external heater (4), a stainless steel proportional flow counter (5) with a heater (6) (heating the detector prevented sorption of the gases recorded by the walls of the counter), a trap for unreacted vapours (7), a system for introducing a quenching additive (8), a rheometer for measuring the total gas flow rate (9), and an recording system. Fractional release or release rate (noble gas flux) can be measured in experiments where the inert gas release is studied. The heating at various temperatures for a definite time, so called isothermal step-heating or isocronal heating, or heating in conditions of increasing temperature are usually employed.

In the analysis of gas mixtures there is usually no need to use the column (2). In the case of vapours that may change the counting characteristics the latter must be converted into a convenient form for recording (for example, the vapours of organic substances labelled in the carbon into CO_2, water into H_2 or C_2H_2 etc.). The conversion conditions must exclude sorption and give both a rapid response and a high degree of conversion of the vapours.

LABELLING OF SOLIDS SAMPLES BY THE NOBLE GASES

Most of the solids to be investigated by RIGDiP do not naturally contain radioactive inert gas and it is necessary to label them with a trace amount of the noble gas. In RIGDiP the labelling of sample can be performed either by introduction of inert gas atoms (TRIGRA) or by the introduction of their parent radionuclides, which serve as a quasi-permanent source of the inert gas atoms (ETA).

Diffusion technique is based on the diffusion of the inert gas into solids at elevated temperatures and pressure of the gas. There is no great difficulty in introducing an inert gas into an organic solid, such as a polymer: good results are given for example by sorption apparatus. However, the rare gases are highly mobile in polymers, which can lead to major complications associated with gas loss during manipulation. If the gas

probe is high mobile, special measures must be taken to retain the gas: cooling to low temperatures, using of gate valves to displace the specimen rapidly from the saturation chamber to the outgassing one, and so on, while high heating rates have to be used starting from liquid-nitrogen temperature.

The bombarded of the sample surface by accelerated ions of inert gases are mainly used. Equipment included two techniques for ion bombarded of solids. In one of them ionised atoms of noble gases are accelerated with high voltage, in other ionisation and acceleration of gas atoms occur in a discharge. The amount of inert gas introduced and its concentration profile depends on the energy of ion, bombarded and the properties of the labelled matrix. Trace amount of ^{226}Ra can be introduced into the sample by coprecipitation during the sample preparation from a solution or adsorption on the surface of the sample. ^{222}Rn is formed by spontaneous alpha decay of radium and can be introduced into the solid owing to the recoil energy. Radon atoms penetrate several tens of nanometers, depending on the composition of the target materials.
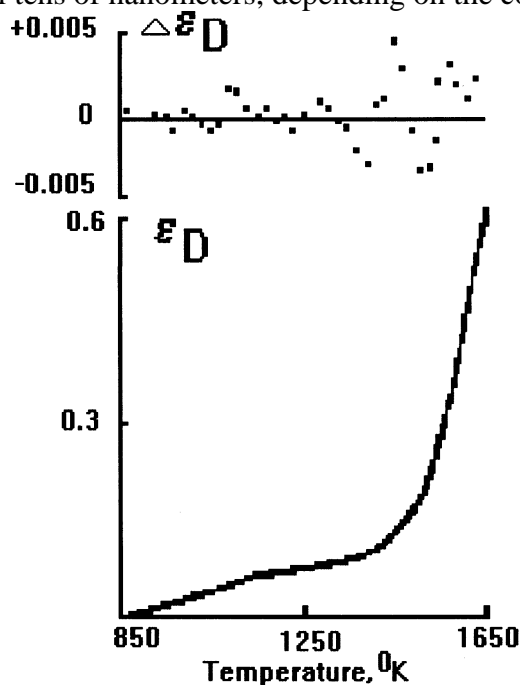

Fig.3. TRIGRA ofY$_2$O$_3$ (Comparison emanation model with experiment). Line - calculation, points-experiment. Upper part of Figure, remainder drift, $\Delta\varepsilon=\Delta\varepsilon_{D, \ exp \ -\Delta\varepsilon D, \ theor}$ (calculated with allowance for. Eq.(14), ordinate scale increased 100-fold).

Method introducing the parent nuclide of inert gas consists in the incorporation of a parent nuclide producing the inert gas into the solid. The introduction of the parent atoms into the labelled solid is accomplished by common crystallization or co-precipitation from the solution containing the radioactive parent nuclide(^{228}Th and ^{224}Ra) in trace concentrations. The distribution of the incorporated parent should obviously be uniform if it can be built isomotphously into the crystal lattice. In cases where there is no possibility of introducing the parent nuclide during the preparation of the sample the impregnation technique can be used. This technique consists in treating a substance to be labelled with a solution containing the radioactive parent nuclides (^{228}Th and ^{224}Ra). ^{228}Th parent atoms are present after labelling by impregnation technique only on the surface of the solid. The daughter products ^{224}Ra and ^{220}Rn are immediately after their generation injected, as the result of their recoil, into the depth of the grains. The maximum depth of penetration of ^{220}Rn achieves two path lengths of the recoil in the given substance. This technique usually yields a non-uniform distribution both of the parent nuclides and the inert gas atoms in the solid. By heating solids to high temperatures, up to melting, the initially non-uniform distribution of the parent nuclides

obtained by the impregnation technique can be changed to the uniform one.

EVALUATION OF TRIGRA AND EGA EXPERIMENTAL DATA AND MODELLING OF THE GAS EVOLUTION

The computer is used in the control ofRIGDiP equipment operation and in evaluation of the results. A set of computer programmes called DIGS (diffusion of inert gas in solids) for the statistical treatment and interpretation of the results of various diffusion methods (permeability, sorption, desorption, thermodesorption spectroscopy, TRIGRA, ETA, etc.) was designed [3]. Various geometrical shapes of samples (sphere, cylinder, plate) can be taken into account; diffusion coefficients depending on time, concentration and coordinates can be evaluated. A bank of general diffusion models has been organized on the basis of both analytical and numerical solutions of diffusion cases.
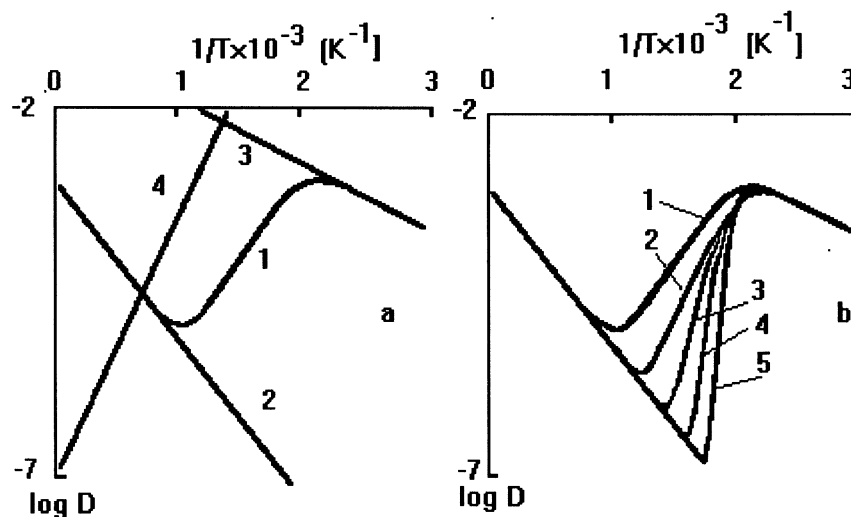

Fig.4. Arrehenius functions of effective diffusion coefficient, calculated by Eqs. (9)-(12) with allowance for Eqs.(13) and (14). $D_1=10^{-3}$ m^2/sec, $E_1=41.8$ kJ/mole, $D20=10^{-1}$ m^2/sec, $E_2=16.7$ kJ/mole, $K_0=10^{-7}$ m^2/sec, $\Delta H_K=16.7$ kJ/mole,

a) Calculation of dissociation of superstoichiometric defect-radon complexes (at constant number of defects, Eq.(13): 1) $D_{eff}(T)$, 2) $D_1(T)$, 3) $D_2(T)$, 4) Keff(T).

b) Calculation of complex dissociation and change in number of defects (Eq.14), (effect of constant CT, with of temperature range of defect annealing, at constant temperature (500°K) on maximum rate of complex dissociation: 1-without dissociation, 2-σ =2, 3-σ=5, 4-σ=10, 5-σ=20.

The set of the programmes involves four parts that give following possibilities:

-preliminary treatment of experimental results (Testing experimental equipment, reconstruction of "non-distorted" TRIGRA and ETA curves)

-evaluation of the results on the basis of the classical diffusion model (functional scales for linearizing non-linear dependencies between the parameters investigated, method of particular points, etc.)

-choice of a more suitable phenomenological model (method of statistical parameters and "diffusion map", least square method)

-choose of a suitable physical model

In the case that the experimental data treated so far do not correspond to the model of classical diffusion, another more adequate model has to be chosen. The choice of an adequate diffusion model is made by a step-wise trial of various models, starting from a simple to more complication ones. In the bank of phenomenological models analytical and numerical solutions of diffusion equations are stored, taking into account irreversible and reversible chemical reactions of the 1st and 2nd order between the gas

and traps in the solid, various cases of parallel diffusion taking into account the exchange of diffusing gas between the diffusion gas between the diffusion channels, etc. In solutions to the diffusion equations various concentrations' profiles of the gas in the solid, various concentration and time dependencies of the diffusion parameters, etc. are considered. The choice of an adequate phenomenological model of diffusion is made by means of standard methods of mathematical statistics.

The phenomenological theory of the thermostimulated release of gas from solid samples, during constant heating rate was used for mathematical simulation of the temperature dependencies of inert gas probe release rate from materials, labelled by radioactive inert gases by ion bombarded or diffusion technique. The experimental curves of the temperature dependencies of the inert gas release were analysed by several methods, such as the method of functional scales, the analyses of the temperature dependencies of the inert gas release effective activation energy, the analysis of the dependence of the pre-exponential factor on the activation energy, method statistical parameters etc.

The THERMOKIN software package makes it possible to simulate the solid state reactions, to evaluate and interpretate of results of various thermal analysis methods such as TG/DTG, DSC, DTA, EGA, etc. The software enabled us to choose the adequate model of solid state reactions, to calculate the parameters of reactions and the errors of the parameters. This software package can be used for optimization and planning of experiments and for the simulation of various mechanisms of solid state reaction [4, 5].

Use of the THERMOKIN software package combined with the set of DIGS package give us the possibility to simulate radioactive inert gas release from solids at various experimental conditions and evaluation of EGA, TRIGRA and EGA experimental data obtained either isothermally at various temperatures or non-isothermally at various heating rates.

The DIGS-THERMOKIN software packages were used in modelling to simulate the thermal decomposition reaction. The transport of gaseous products taking place during thermal decomposition reactions was considered in the framework of percolation theory. Mathematical modelling makes it possible to understand the role of irregular morphology in non-steady state solid state reactions and diffusion processes taking place in disordered structures.

This theory makes it possible to explain a number of experimentally observed effects, such as

- the threshold character of gas escape from the thermally decomposed solids,

- the loss of sample compactness and the grain size distribution of the reaction products

- the disagreement between experimentally observed TG (DTG) and EGA curves and the formal kinetics curves of the solid state process corresponding to the reaction mechanism supposed. The fractal geometry methods were used in the characterization of the heterogeneous material. Following characteristics of the thermal decomposition kinetics were calculated:

-time dependence of the volume fraction of initial phase;

-time dependence of the portion of the newly formed highly disordered phase - time dependence's of the mass of sample;

-time dependence's of the flux of the reaction products released from the sample;

-time dependence's of the flux of the radioactive inert gases previously introduced into the sample (TRIGRA-curve)

-Time dependence's of the release of the radioactive inert gas (220Rn) fi-om samples labelled by the parent nuclides (emanation release rate, ETA-curve)

APPLICATION OF ETA and TRIGRA IN MATERIAL SCIENCE

The inert radioactive gases were advantageously used as the probe of the defect state of solids, such as non uniformity of their structures, presence of various type of structure defects and the changes of their concentration in the solids.

1. Generation and annealing of defects in solids

In the our work radon-220 diffusion coefficients in polycrystalline Y_2O_3 have been determined by ETA [6]. For Y_2O_3 synthesis the starting material was yttrium hydroxide obtained by precipitation with ammonium hydroxide from yttrium nitrate. At the moment of precipitation thorium-228, the parent radionuclide of radon-220, was added. ^{228}Th comprecipitated quantitatively with $Y(OH)_3$. Then the $Y(OH)_3$ powder was stored in a box for a month in order to establish radioactive equilibrium in the series:

$$^{228}Th \xrightarrow[T=1,9\,лет]{\alpha} \; ^{224}Ra \xrightarrow[T=3,6\,дн.]{\alpha} \; ^{220}Rn \xrightarrow[T=54,5\,сек]{\alpha}$$
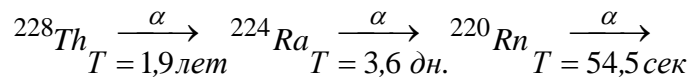
The samples were heated at 10 deg/min in a stream of air or argon in a unit for comprehensive emanation thermal analysis [7]. Simultaneously there were recorded curves for rate of radon-220 evolution (ETA), and for DTA, TGA, and the change of linear dimensions of the $Y(OH)3$ powder core (dilatometric curve). The sample was held at maximum test temperature (1693-1723K) for 30 min, then cooled in the furnace with simultaneous recording of all curves. With the first heating, yttrium hydroxide decomposed to form Y.203, as shown by the peaks in the ETA and DTA curves and weight loss and shrinkage of the sample. During the second and subsequent heatings the ETA curves do not record any sort of change in the sample. Subsequently we will consider the ETA curves for well annealed yttrium oxide that were obtained during the third heating.

Because of the reversibility of the ETA curves during the second and subsequent heatings and coolings of Y203 at room temperature is determined by the flow of radon-220 atoms, SR, originating during radioactive decay from radium-224, while there is practically contribution to emission under these conditions. Since SR is much less than 35% (about 1%), the effective powder granule size ro can be calculated by the equation [8]:

$$r_0 = \frac{3}{4}\frac{\overline{R}}{\varepsilon_R} \tag{1}$$

where R is range of atoms produced by radon-220. CR-recoil emanating power. The range R is calculated by the formula [8]:

$$\overline{R} = 83\frac{1}{\rho}\frac{\overline{A}}{B} \; [10^{-4}\text{ m}]. \tag{2}$$

where A is the average atomic weight of the substance; p is density, g/cm^3; B is stopping power. In yttrium oxide the range of output was 3.45xl0-8m. The difference between CT and CR is the diffusion contribution ε_D of radon-220 to the emission capability of yttrium oxide. Since for Y_2O_3 powder the particle size ro is much larger than the range of output R, the following relation is fulfilled with good approximation for all ST) values [8]:

$$\varepsilon_D = \frac{3}{y}(\text{cthy} - \frac{1}{y}), \tag{3}$$

here $y = r_0\sqrt{\lambda/D}$, λ is the radon-220 decay constant (0.0127 sec^{-1}), D is the effective diffusion coefficient of radon in the sample matrix, and E_D-difrusion emanating power.

As the temperature rises the emission capability of yttrium oxide first stays

practically constant (diffusion does not contribute substantially at low temperature to emission by this oxide) (Fig.3). Then at 770-1150K emission increases sharply due to the diffusion contribution, while in the 1170-1420K range it is practically independed of temperature. Over the 770-1420K range the diffusion mobility of radon-220 is anomalously high, because according to the theory of [8], a substantial diffusion contribution to emission should be expected only at temperatures more than 0.5K above the absolute melting point, which for yttrium oxide is 1349K. Above 1420K yttrium oxide emission again increase and follows the usual exponential rule (Fig.3). The Y_2O_3 emission curves during heating and cooling completely. The nature of Y_2O_3 emission in an argon atmosphere is analogous to that described for an air atmosphere (oxygen partial pressure 1 and 0.2×10^5 Pa respectively).
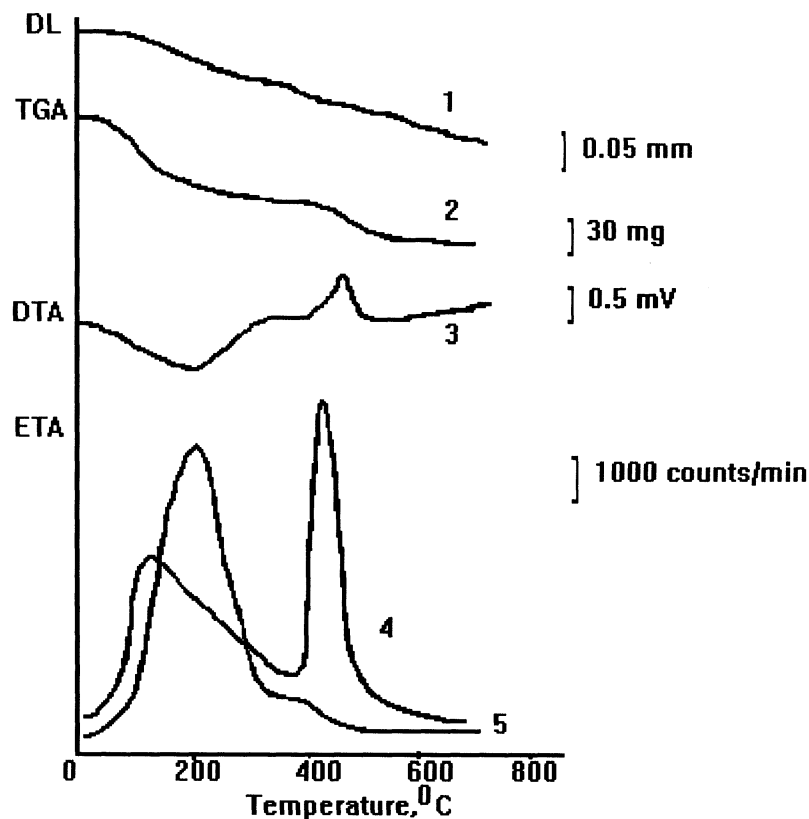

Fig.5. Combined emanation-thermal analysis of titanium hydroxide.
1-dilatometric analysis, 2-thermogravimetric analysis, 3-differential thermal analysis, 4-temperature dependence of the rate of radon release, 5-temperature dependence of the rate of release of water labelled with ^3H.

To explain this pictures of emission by nonstechiometric oxide we proposed a mathematical model of noble gas diffusion [6]. It is assumed that the complicated nature of Y_2O_3 emission is due to at least two mechanism of radon diffusion that are related to the two possible states of radon in the Y_2O_3 crystal lattice. Radon is distributed between "high temperature" and "low temperature" defects to form, as it was, complexes, vis., h.d.(Rn) (radon is a "high temperature defect") and l.d.(Rn) (radon in a "low temperature defect"). In the h.d.(Rn) complex's radon diffusion has a high activation energy, so that it predominates at high temperature, whereas in l.d.(Rn) complex the activation energy is low and diffusion predominates at lower temperature.

It is assumed that the concentration of easily mobile low temperature complexes is determined by the concentration of superstoichiometric oxygen in the yttrium oxide lattice. In the first version of the proposed model (hypothesis A) the concentration of low temperature defects is taken as constant; in the more complete version (hypothesis

B) account is taken of the change in the number of low temperature defects related to the change in nonstoichiometry of yttrium oxide occurring over a narrow temperature range.

As the temperature increases, so does the mobility of the low temperature complexes, and the emission capability of yttrium oxide increases correspondingly. The dissociation of these complexes also increases so that a larger and larger portion of the radon is present in a low-mobile state (the h.d.(Rn) high temperature complexes).

Let us describe the reversible formation of easily mobile radon complexes by:

$$h/d/(Rn) + l.d.(0) \xrightleftharpoons[k_2^*]{k_1^*} h.d.(0) + l.d.(Rn), \tag{4}$$
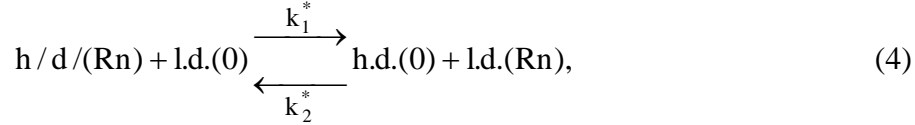
Where h.d.(Rn) is radon in a high temperature low-mobile defect; l.d.(O) is an unoccupied low temperature defect; h.d.(O) is an unoccupied high temperature defect; l.d.(Rn) is radon in a low-mobile complex; k_1^* is the rate constant for l.d.(Rn) complex formation; k_2^* is rate constant for l.d.(Rn) complex decomposition.

At thermal equilibrium we can introduce the equilibrium constant K of the reversible redistribution of radon between low temperature and high temperature defects. We shall assume that the defects are at thermal equilibrium; i.e., $N_1+N_2=N$, where N_1 is the concentration of high temperature defects; N_2 is the concentration of low temperature defects; and N is the total defect concentration. The formation constant of the l.d.(Rn) complex is:

$$K^* = \frac{C_2 N_1(0)}{C_1 N_2(0)} = \frac{C_2(N_1 - C_1)}{C_1(N_2 - C_2)} = \frac{k_1^*}{k_2^*} \tag{5}$$

where Ci and C^ are Rn concentrations in high temperature and low temperature defects, respectively; and NI(O) and N3(0) are the concentrations of the respective unoccupied defects.

In the emission method ultra small radon concentrations are used, so that Ci«Ni and C2«N2. Then

$$K^* \frac{C_2}{C_1} = \frac{k_1^* N_2}{k_2^* N_1} = \frac{k_1}{k_2}, \tag{6}$$

$$k_{1=}k_1^* N_1; \quad k_{2=}k_2^* N_2$$

Because

$$N_2 \prec\prec N_1 \quad \text{and } N_1 \approx N, \quad \text{then } K^* = KN_2$$

$$\text{where } K = \frac{k_1^*}{k_2^*} \tag{7}$$

The mechanism of transfer by two kinds of diffusion routes between which exchange takes place, formally described by the kinetics of a first order chemical reaction, is designated dissociative diffusion. The system of differential equations that describes such a process has form:

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} - k_1^* \phi_1 C_1 + k_2^* \phi_2 C_2$$

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2} + k_1^* \phi_1 C_1 - k_2^* \phi_2 C_2 \tag{8}$$

where D_1 is the radon diffusion coefficient over the high temperature defects; D_2, over the low temperature defects; $\phi_1=N_1/N_2$ and $\phi_2=N_2/N$ are the relative concentrations of high and low temperature defects, respectively ($\phi_1+\phi_2=1$)

In the presence of local equilibrium ($k_1C_1 = k_2C_2$) tne diffusion process is described by the effective diffusion coefficient:

$$D_{eff} = \frac{D_1 + K\phi_2 D_2}{1 + K\phi_2} \tag{9}$$

The terms of Eq.9 obey the temperature dependencies

$$D_1 = D_{10}\exp(-E_1/RT), \tag{10}$$

$$D_2 = D_{20}\exp(-E_2/RT), \tag{11}$$

$$K = K_0\exp(\Delta H/RT) \tag{12}$$

Where E_1 and E_2 are the activation energies of radon diffusion via the high and low temperature defects respectively; ΔH is the enthalpy of l.d.(Rn) complex formation; D_{IO}, D_{20}, and K_0 are the respective preexponential factors; and R is the gas constant.

A serious problem is present by the correct allowance for the temperature dependence of the concentration of easily mobile low temperature defects $\phi_2(T)$. ϕ_2 is independed of temperature if radon diffusion takes place via impurity defects, or ifl.d.(Rn) complex dissociation is faster than that of the most mobile low temperature defects; $\phi_2(T)$ is a function that diminished during annealing of (e.g., radiation) defects; $\phi_2(T)$ is a stepwise function that decreases over a narrow temperature range if phase transition, change of extent of nonstoichiometry, etc., take place in the solid. To describe the anomalous temperature dependence of the emission capability of yttrium oxide two hypotheses have been used.

(A). The emission process is limited by the kinetics of l.d.(Rn) complex dissociation, i.e.:

$$\phi_2(T) = \text{const.} \tag{13}$$

(B). The emission process is affected both by l.d.(Rn) complex dissociation and by the change in extent of nonstoichiometry of oxide, i.e., changes in ϕ_2. Then

$$\phi_2(T) = \phi_2^0\left(1 - \frac{A}{2}\left\{\text{erf}\left(\frac{T - T_m}{\sqrt{2}\sigma}\right) + 1\right\}\right)$$

or

$$\phi_2(T) = \phi_2^0\left(1 - \frac{A}{2}\{\text{erfz} + 1\}\right) \tag{14}$$

Where ϕ_2^0 is the concentration of difficulty mobile defects before the start of heating; A is constant that determines the concentration range of the transition;

Tin is the temperature of maximum rate of change of oxide nonstoichiometry; c is a constant that determines the temperature range of transition ΔT ($\Delta T = 3\sigma$),

$$\text{erfz} = \frac{2}{\sqrt{\pi}}e^{-\xi^2}\,d\xi; \quad z = \frac{T_1 - T_m}{\sqrt{2}\sigma} \text{ and } \xi \text{ is a variable of integration.}$$

The introduction of hypothesis (B) is based on the experimental fact [9] those yttrium oxide nonstoichiometry changes during heating. At constant oxygen pressure in the gas phase part of the superstoichiometric oxygen is removed, while with cooling under the same conditions it renters the lattice. At constant temperature:

$$Y_2O_{3+m} \Leftrightarrow Y_2O_{3+n} + (n - m)O\uparrow, \tag{15}$$

where n<m<<1

At temperatures of the order of 1200K stoichiometric composition of yttrium oxide is reached only at oxygen partial pressures of 10^{-8}-10^{-16} pa. Therefore at oxygen partial pressures in the gas phase of 1 and 0.2×10^5 Pa in experiments. When ETA was

carried out in a stream of argon or air, respectively, the yttrium oxide lattice always contained superstoichiometric oxygen.

The reversible evolution (or absorption) of oxygen that takes place over a certain temperature range can affect the concentration of low temperature easily mobile defects, ϕ_2. Therefore the temperature dependence ϕ_2 (T) is a function not only of temperature, but also of oxygen partial pressure in the gas phase. Unfortunately at present the exact form of ϕ_2 (T) is not known, but from the date on electrical conductivity it follows [9] that ϕ_2 (T) is a descending S-shaped function. The change in nonstoichiometry at constant partial pressure of oxygen can be considered, to a first approximation, as a diffusion phase transition; over a small temperature range close to the transition point Tm the low temperature phase Y_2O_{3+m} and the high temperature phase Y_2O_{3+m} coexist. The clearest manifestation of the coexistence of the two phases is the gradual, not spasmodic, change of physical properties in the transition region. The theory of diffusion phase transition of the first kind predicts that the temperature dependence of the concentration of the transformed phase (and therefore ϕ_2) can be approximated by Eq.14.
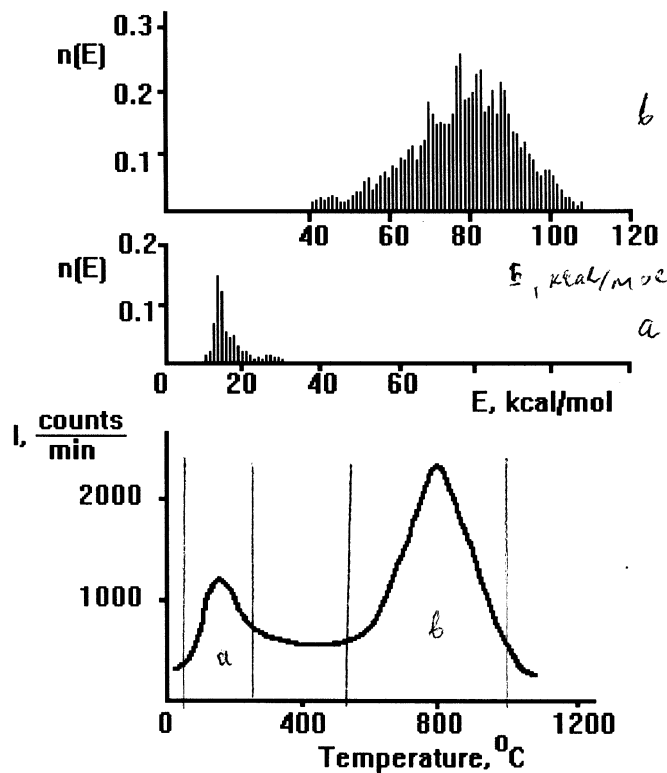

Fig.6. TRIGRA oftitania (anatase)

Upper part: The spectra of radon release activation energy values (parts a and b) determined from the TRIGRA experiments in the diagnostics of anatase sample.

Lower part: The temperature dependence of the thermostimulated radon release from anatase powder. (Heating in air at a heating rate of 5 K/min).

To illustrate the effect of various factors on the temperature dependence of the diffusion coefficient we calculated the D_{eff}(T) functions within the framework of the various hypotheses concerning the temperature dependence ϕ_2. As a example, Fig.4a shows the dependence of $\ln D_{eff}$ on 1/T calculated by Eq.9 with allowance for Eqs.10-13 and various values of ΔH. The low temperature part of the $\ln D_{eff}$ - 1/T plot is an ascending straight line with slope of E_2/R. As the temperature increases the diffusion

coefficient begins to fall sharply (decomposition of the easily mobile l.d.(Rn) complexes), then rises again, but still with slope E_1/R. Thus even in its simplest version A, our model predicts the appearance of peaks or plateau's in the $\varepsilon(T)$ curve.

Fig.4b shows the Arrhenius functions of $D_{eff}(T)$ calculated within the framework of hypothesis (B) (i.e., according of Eq.9 with allowance for Eqs.10-12 and 14) at various values of transition width (i.e., of constant σ). The transition width has a substantial effect on the shape of the emission curves; the narrower the number of defects decreases spasmodically from one value to another the high temperature branch of the peak becomes vertical.

The proposed model of noble gas diffusion in a nonstoichiometric oxide was used to process the results of TRIGRA of yttrium oxide (Fig.3). With the aid of a standard program for non-linear least squares within the frameworks of hypotheses (A) and (B), the parameters of Esq., 9, 10-12 and 13 (six parameters) and Eq.14 (nine parameters) of experimental error both hypotheses are suitable. m the case of model (B) the dispersion is lower, and what is more significant, the systematic remainder drift in the region of the emission "plateau" when the results are adjusted according to model (A) takes on a radon character when the results are processed according to hypothesis (B). It should also be noticed that the temperature range of transition obtained by calculation corresponds to that found by the electrical conductivity method [9]. Therefore to us hypothesis (B) appears better grounded physically.

It is of interest to compare the parameters of radon-220 diffusion in yttrium oxide with those of oxygen and yttrium self-diffusion. Table 2 shows the self-diffusion parameters of oxygen and yttrium and the radon diffusion parameters as well as the diffusion coefficients D_O, D_y, and D_{Rn} calculated from those parameters at 1673K. The last column of Table 2 shows that the high temperature (1673K) mobility of radon-220 in yttrium oxide is close to that of cations, although the mechanisms of their diffusion are probably different because the diffusion parameters are substantially different. It was shown [10] that over a certain range of oxygen partial pressure ($l-0.5 \times 10^5$Pa), as the temperature is raised the predominant type of ionic defect in the yttrium oxide structure changes; up to 1220K it is mainly O_i'', while above 1220K it is V_y. It can be concluded that Rn-220 diffusion in Y_3O_3 at temperatures up to 1220K takes place via the easily mobile complex with O_i'', participation, while above 1470K it is via complexes that involve V_Y'', and in the intermediate region both mechanisms are present.

2 The study of dehydration processes of hydroxides

In our work [2] the dehydration process of titanium hydroxide have been investigated by TRIGRA. The titanium hydroxide was obtained by hydrolysis of $TiCl_4$ with an aqueous solution of ammonia. For studying the dehydration processes in amorphous titanium hydroxide a radioactive tracer (^3H_2O) was introduced. Radon was introduced into tritium-labelled titanium hydroxide by gas labelling in a high-frequency discharge by means a Tesla transformer.

The titanium hydroxide with double radioactive labelling was placed in a reactor in an electrical furnace (see Fig.2), which gave a linear rise in temperature of 7.5 deg/min. The decomposition product and radon were extracted with a stream of carrier gas (helium), passed into the column (2), packed with a mixture of calcium carbide and pumice, heated to 1200C, where the reaction of the water vapour with CaC_2 gave acetylene, and finally into a trap with sulphuric acid. During the experimental there was continuos and simultaneous determination of the concentrations of C_2T_2 and ^{222}Rn in the gas by means the recording system for spectroscopic analysis of energetic pulses emerging from flow detector.

Figure 5 gives the data for combined investigation of decomposition of titanium hydroxide, including TGA, DL, and DTA, and the relation of the rate of evolution of

radon and water to the sample temperature under conditions of continuous heating. As curve 1 shows (DL), the decomposition of the hydroxide is accompanied by a decrease in the linear dimensions of the sample right up to 800°C. The loss in weight of the sample (curve 2) occurs over two temperature ranges: 20-400°C and 400-650°C. Curve 3 (DTA) records a low-temperature endo effect at 205° (dehydration) and an exo effect of crystallisation at 450°C. The temperature dependence of the rate of radon evolution (curve 4) shows two gas evolution maxima (125 and 430°C). The region of the maximum rate of radon release is considerably ahead of the maximum rate of water evolution (215°C, curve 5) and slightly ahead of the crystallization maximum (450°C, DTA). This is in complete accords with the topochemical character of the dehydration and crystahzation processes. The dependencies obtained show that hardly any evolution of water is observed in the crystallization process.

The TRIGRA of tritium labelling hydroxides makes it possible to compare the rate of release of the radioactive inert gas probe with the rate of dehydration. This is extremely important in calculations of the parameters of the diffusion of gases in solids in the region of solid-phase reactions.

3 Characterization of thermal behaviour of titania

TRIGRA was used in the characterization of thermal behaviour of titania (anatase) [13]. The experimental results were treated by means of the DIGS software using the "single-jump diffusion" model. The oxide samples prepared by heating of titanium hydroxide at 550°C in a stream of air. The radon was introduced into the surface near layers of titania in the low temperature glow discharge according to Jech [14].

By heating the radon bombarded anatase the radiation effects and solid-state transformations are accompanied by the release of inert gas. As it is seen in Fig.6 , Curve 1, two effects on the TRIGRA-curve of TiO_2-anatase are observed: first in the temperature range 140-180°C, believed as corresponding to the release of inert gas atoms located at positions, where the diffusion path was shortened by the bombardment; second - in the temperature range 600-900°C believed to be caused by anatase-rutile transformation. A volume shrinkage is observed on the dilatometric curve in the temperature ranges 100-550 and 550-1000°C. DTA recorded one endo effect (120°C). The anatase-rutile phase change is not reflected on the DTA.

The radon release from anatase at the temperature within the range 20-350°C (see Fig. 6 -the temperature interval denoted a) corresponds activation energy the radon release spectrum (spectrum a), where the E_{min}=17 kcal/mol, E_{mean}=19 kcal/mol, E_{max}=22 kcal/mol. The radon release rate at the temperature within range anatase-rutile transformation (600-900°C) characterized be a wide spectrum of the activation energies of radon release: E_{min}=40 kcal/mol, E_{mean} =83 kcal/mol, E_{max} = 111 kcal/mol (the energy spectrum b). The activation energy values determined from experimental results of TRIGRA correlate well with that of phase transformations: the inert gases release kinetic is controlled by the kinetic of solid state processes.

CONCLUSION

Where the method radioactive inert gas diffusion probe has been used to investigate solid state processes we stated higher sensitivity of diffusion analysis than DTA or X-ray patterns. The results obtained in this work can be used for the application of this method not only in the investigation of thermal decomposition processes used e.g. for production of oxides, but also in the investigation of disordered solid e.g. their transition from the metastable disordered stage to a more stable ordered stages. The methods presented in this paper can be used for the investigation of the other types of the reactions of solids, e.g. based on the solid-gas or solid-liquid interactions.

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Table 1. Evolution of results of Y_2O_3 TRIGRA experiment

Hypo-thesis	$\ln\frac{D_{10}}{r_0^2}$	E_l kJ/mol	$\ln\frac{D_{10}}{r_0^2}$	E_2 kJ/mol	InK_o	ΔH_K kJ/mol	Tm, K	$\Delta T.K$	A (rel. units)
A	23.5	419	3.2	129	-11.9	103			
B	27.8	475	21.0	250	-23.6	165	1200	246	0.63

Table 2. Diffusion parameters of O [11], Y [12], and ^{220}Rn (present work) in Yttrium Oxide, and diffusions coefficients of these species calculated for 1673^0R.

Diffusion species	Themperature range, °K	DO, m2/sec	E, kJ/mole	D at 1673 °K, m2/sec
Oxygen	1273-1773	7.3x10-2	191	0.81x10-7
Yttrium	1673-1973	1.48x10-4	289	0.15x10-14
Radon-220	1533-1673	3.8	475	0.58x10-14