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# DIFFUSION OF RADON-220 IN YTTRIUM OXIDE

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Effective diffusion coefficients of radon-220 in yttrium oxide were determined by emission thermal analysis. To explain the anomalous course of the emission thermal curve a new model is proposed for radon diffusion in $Y_2O_3$ that describes a complex process proceding via two paths with interchange, and takes account of the decreased defect concentration in the low-temperature path when the temperature is increased. For the first time, parameters of concentration change of low-temperature defects were determined, diffusion parameters of radon-220 in $Y_2O_3$ were calculated, and diffusion coefficients of radon-220, oxygen, and yttrium were compared.

Yttrium oxide is used in various new technologies, particularly in nuclear power engineering as an additive to fuel elements and as a structural material for nuclear reactors (thanks to its low cross section for slow electron capture and its high refractoriness) [1]. It was therefore of interest to study the diffusion of heavy noble gases in $Y_2O_3$. Moreover the diffusion of radioactive noble gases is a sensitive structural probe [2] by which the generation and annealing of defects in solids can be followed.

The evolution of the heavy noble gas radon-220 (thorium emanation) from yttrium oxide has been studied in [3]. An anomalously high mobility of radon-220 was found at temperatures up to 1423°K. By comparison with electrical conductivity measurements and oxygen evolution from yttrium oxide when heated in vacuum, this phenomenon was explained by a change in the extent of nonstoichiometry of yttrium oxide.

In the present work radon-220 diffusion coefficients in polycrystalline $Y_2O_3$ (fine powder) has been determined by emission thermal analysis (ETA) [4]. Primary attention has been paid to the development of a mathematical model of radon diffusion and to comparison of the measured temperature dependence of the radon diffusion coefficient with that calculated from the new model.

For $Y_2O_3$ synthesis the starting material was yttrium hydroxide obtained by precipitation with ammonium hydroxide from 0.2 M yttrium nitrate at pH 9. At the moment of precipitation thorium-228, the parent radionuclide of radon-220, was added. $^{228}Th$ coprecipitated quantitatively with $Y(OH)_3$, while $^{224}Ra$ stayed entirely in the filtrate. The precipitate was washed twice with distilled water, filtered under vacuum, and dried in air for three days. Then the $Y(OH)_3$ powder was ground in a mortar and stored in a box for no more than a month in order to establish radioactive equilibrium in the series:

$$\underset{T=1.9\text{ yr}}{^{228}Th} \xrightarrow{\alpha} \underset{T=3.6\text{ days}}{^{224}Ra} \xrightarrow{\alpha} \underset{T=54.5\text{ sec}}{^{220}Rn} \xrightarrow{\alpha} .$$

The concentration of parent radionuclide was $\sim 10^{-11}$ g/g. According to spectral analysis, yttrium oxide prepared by this method contained the following impurities: Mg 0.001, Si 0.001. Ti 0.003 wt.%.

The samples were heated at 10 deg/min in a stream of air or argon in a unit for comprehensive emission thermal analysis [5, 6]. Simultaneously there were recorded curves for rate of radon-220 evolution from its α-radioactivity (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 (1693-1723°K) for 30 min, then cooled in the furnace with simultaneous recording of all curves. With the first heating, yttrium hydroxide decomposes to form

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TABLE 1.

| Hypothesis | $\ln \frac{D_{10}}{r_0^2}$ | $E_1$, kJ/mole | $\ln \frac{D_{20}}{r_0^2}$ | $E_2$, kJ/mole | $\ln K_0$ | $\Delta H_K$, kJ/mole | $T_M$, K | $\Delta T$, K | A (rel. unit) |
|---|---|---|---|---|---|---|---|---|---|
| A | 23.5 | 419 | 3.2 | 129 | —11.9 | 103 | 1200 | 246 | 0.63 |
| B | 27.6 | 475 | 21.0 | 250 | —23.6 | 165 | | | |

TABLE 2. Diffusion Parameters of O [11], Y [12], and $^{220}$Rn (present work) in Yttrium Oxide, and Diffusion Coefficients of These Species Calculated for 1673°K

| Diffusing species | Temperature range, °K | $D_0$, $m^2$/sec | E, kJ/mole | D at 1673°K, $m^2$/sec |
|---|---|---|---|---|
| Oxygen | 1273—1773 | $7.3 \cdot 10^{-2}$ | 191 | $0.81 \cdot 10^{-7}$ |
| Yttrium | 1673—1973 | $1.48 \cdot 10^{-4}$ | 289 | $0.15 \cdot 10^{-14}$ |
| Radon-220 | 1533—1673 | 3.8 | 475 | $0.58 \cdot 10^{-14}$ |

$Y_2O_3$, 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 for heating and cooling are completely reversible, while the DTA, TGA, and dilatometric 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.

It should be noted that the ETA curves record the radon-220 flow, j, whereas the theory was developed [4] for the emission capability of a substance, ε. The latter is determined by the ratio of the rate of radioactive gas evolution to that of its formation in the solid from the decaying parent radionuclide. To go from j to ε, i.e., to normalize the flow to the rate of radon-220 formation, is possible by the use of a high-emitting $^{228}$Th preparation (barium stearate coprecipitated with thorium-228) the efficiency of the radon-220 count from a dry sample was determined, and by means of a liquid reference material (solution of thorium-232 equilibrium salt) the efficiency of the count from the solution was determined. Then under the same conditions the emission from an aliquot of sample was measured, whence the absolute specific activity of the latter was calculated.

Because of the reversibility of the ETA curves during the second and subsequent heatings and coolings of $Y_2O_3$ we were able to assume that the experiments were carried out under quasiequilibrium conditions; we therefore used normalization of radon flow with respect to absolute radioactivity of each current temperature, $\varepsilon_T$. At this point a correction was introduced for the time lag of the recording apparatus.

The emission capability of $Y_2O_3$ at room temperature is determined by the flow of radon-220 atoms, $\varepsilon_R$, originating during radioactive decay from radium-224, while there is practically no diffusional contribution to emission under these conditions. Since $\varepsilon_R$ is much less than 35% (about 1%), the effective powder granule size $r_0$ can be calculated by the equation [4]:

$$r_0 = \frac{3}{4} \frac{\bar{R}}{\varepsilon_R}, \quad (1)$$

where $\bar{R}$ is the range of atoms produced by radon-220. The range is calculated by the formula [4]:

$$\bar{R} = 83 \cdot 1/\rho \, [\bar{A}/B] \quad [10^{-10} \text{ м}], \quad (2)$$

where $\bar{A}$ is the average atomic weight of the substance; ρ is density, g/cm$^3$; B is stopping power. In yttrium oxide the range of output was $3.45 \cdot 10^{-8}$ m. The difference between $\varepsilon_T$ and $\varepsilon_R$ is the diffusional contribution $\varepsilon_D$ of radon-220 to the emission capability of yttrium

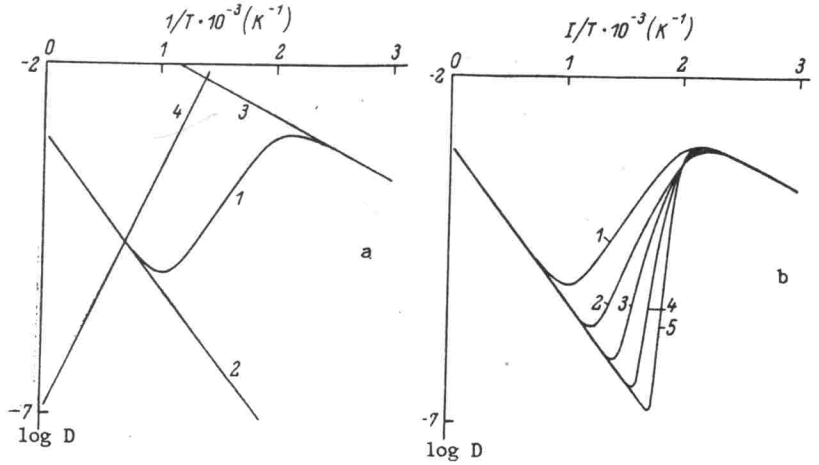


Fig. 1. Arrhenius functions of effective diffusion coefficient, calculated by Eqs. (9)-(12) with allowance for Eqs. (13) and (14). $D_{1o} = 10^{-3}$ m²/sec, $E_1 = 41.8$ kJ/mole, $D_{2o} = 10^{-1}$ m²/sec, $E_2 = 16.7$ kJ/mole, $K_o = 10^{-7}$, $\Delta H_k = 16.7$ kJ/mole. a) Calculation of dissociation 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) $K_{eff}(T)$. b) Calculation of complex dissociation and change in number of defects (Eq. (14)), (effect of constant $\sigma$, width of temperature range of defect annealing, at constant temperature (500°K) on maximum rate of complex dissociation: 1) without dissociation, 2) $\sigma = 2$, 3) $\sigma = 5$, 4) $\sigma = 10$ 5) $\sigma = 20$.

oxide. The ratios that relate $\varepsilon_D$ to the emission diffusion coefficient in a solid are known [4]. Since for our $Y_2O_3$ powder the particle size $r_o$ is much larger than the range of output R, the following relation is fulfilled with good approximation for all $\varepsilon_D$ values [4]:

$$\varepsilon_D = \frac{3}{y}\left(\operatorname{cth} y - \frac{1}{y}\right), \qquad (3)$$

here $y = r_o\sqrt{\lambda}/D$, $\lambda$ is the radon-220 decay constant (0.0127 $sec^{-1}$), and D is the effective diffusion coefficient of radon in the sample matrix. Our experiments were processed using Eq. (3) with specially written program on a SM-14 computer.

As the temperature rises the emission capability of yttrium oxide first stays practically constant (emission due to radioactive decay is independent of temperature, and diffusion does not contribute substantially at low temperature to emission by this refractory oxide). Then at 770-1150°K emission increases sharply due to the diffusional contribution, while in the 1170-1420°K range it is practically independent of temperature. Over the 770-1420°K range the diffusional mobility of radon-220 is anomalously high, because according to the theory of [4], a substantial diffusional contribution to emission should be expected only at temperatures more than ∿0.5° above the absolute melting point, which for yttrium oxide is 1340°K. Above 1420°K yttrium oxide emission again increases and follows the usual exponential rule. The $Y_2O_3$ emission curves during heating and cooling coincide 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 $0.2 \cdot 10^5$ Pa respectively). We explain this by the similarity of yttrium oxide defect structures at the specified partial pressures of oxygen.

To explain this picture of emission by nonstoichiometric oxide we propose a mathematical model of noble gas diffusion. It is assumed that the complicated nature of $Y_2O_3$ emission is due to at least two mechanisms 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 were, complexes, viz., h.d.(Rn) (radon in a "high temperature defect") and l.d.(Rn) (radon in a "low temperature defect"). In the h.d.(Rn) complexes radon diffusion has a high activation energy, so that it predominates at high temperature, whereas in l.d.(Rn) complexes the activation energy is low and diffusion predominates at lower temperature.

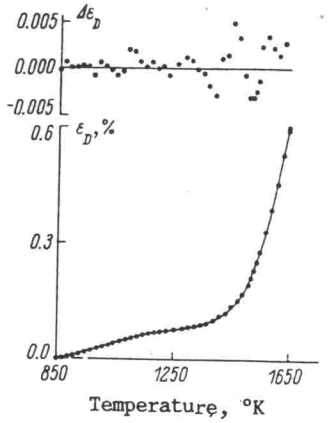


Fig. 2. Comparison of $Y_2O_3$ emission model with experiment. Line) calculation; points) experiment; upper part of Figure, remainder drift, $\Delta\varepsilon = \varepsilon_D - \varepsilon_{D_{theor}}$ (calculation with allowance for Eq. (14), ordinate scale increased 100-fold).

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 variant of the proposed model (hypothesis A) the concentration of low temperature defects is taken as constant; in the more complete variant (hypothesis B) account is taken of the change in the number of low temperature defects related to the change in non-stoichiometry of yttrium oxide occuring 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. But 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 move on to a mathematical description of the proposed radon diffusion mechanism. Let us describe the reversible formation of easily mobile radon complexes by:

$$\text{h. d. (Rn)} + \text{l. d. (0)} \underset{k_2^*}{\overset{k_1^*}{\rightleftarrows}} \text{h. d. (0)} + \text{l. d. (Rn)}, \tag{4}$$

where h.d.(Rn) is radon in a high temperature low-mobile defect; l.dl(0) 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 constan for l.d.(Rn) complex formation; $k_2^*$ is the 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:

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

where $C_1$ and $C_2$ are Rn concentrations in high temperature and low temperature defects, respectively; and $N_1(0)$ and $N_2(0)$ are the concentrations of the respective unoccupied defects.

In the emission method ultrasmall radon concentrations are used, so that $C_1 \ll N_1$, and $C_2 \ll N_2$. Then

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

$$k_1 = k_1^* N_1;\ k_2 = k_2^* N_2.$$

Because

$$N_2 \ll N_1 \text{ and } N_1 \simeq N, \text{ then } K^* = KN_2 \tag{7}$$

where $K = k_1^*/k_2^*$.

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 [4]. The system of differential equations that describes such a process has the form:

$$\begin{cases} \dfrac{\partial C_1}{\partial t} = D_1 \dfrac{\partial^2 C_1}{\partial x^2} + k_1^* \Phi_1 C_1 + k_2^* \Phi_2 C_2, \\ \dfrac{\partial C_2}{\partial t} = D_2 \dfrac{\partial^2 C_2}{\partial x^2} + k_1^* \Phi_1 C_1 - k_2^* \Phi_2 C_2, \end{cases} \tag{8}$$

where $D_1$ is the radon diffusion coefficient over the high temperature defects; $D_2$, over the low temperature defects; $\Phi_1 = N_1/N$ 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 ($k_1 C_1 = k_2 C_2$) the diffusion process is described by the effective diffusion coefficient:

$$D_{\text{eff}} = \frac{D_1 + K\Phi_2 D_2}{1 + K\Phi_2}. \tag{9}$$

The terms of Eq. (9) obey the temperature dependences.

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

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

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

where $E_1$ and $E_2$ are the activation energies of radon diffusion via the high and low temperature defects respectively; $\Delta H_E$ is the enthalpy of $\ell$.d.(Rn) complex formation; $D_{10}$, $D_{20}$, and $K_0$ are the respective preexponential factors; and R is the gas constant.

A serious problem is presented by the correct allowance for the temperature dependence of the concentration of easily mobile low temperature defects $\Phi_2(T)$. $\Phi_2$ is independent of temperature if radon diffusion takes place via impurity defects, or if $\ell$.d.(Rn) complex dissociation is faster than that of the most mobile low temperature defects; $\Phi_2(T)$ is a function that diminishes during annealing of (e,g., radiational) 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 $\ell$.d(Rn) complex dissociation, i.e.:

$$\Phi_2(T) = \text{const}. \tag{13}$$

(B). The emission process is affected both by $\ell$.d.(Rn) complex dissociation and by the change in extent of nonstoichiometry of oxide, i.e., changes in $\Phi_2$. Then:

$$\Phi_2(T) = \Phi_2^0\left(1 - \frac{A}{2}\left\{\operatorname{erf}\left(\frac{T - T_{\text{м}}}{\sqrt{2}\,\sigma}\right) + 1\right\}\right)$$

or

$$\Phi_2(T) = \Phi_2^0\left(1 - \frac{A}{2}\{\mathrm{erf}\, z + 1\}\right), \tag{14}$$

where $\Phi_2^0$ is the concentration of difficulty mobile defects before the start of heating; A is a constant that determines the concentration range of the transition; $T_m$ is the temperature of maximum rate of change of oxide nonstoichiometry; $\sigma$ is a constant that determines the temperature range of transition $\Delta T$ ($\Delta T = 3\sigma$) $\mathrm{erf}\, z = 2/\sqrt{\pi}\, e^{-\xi^2} d\xi$; $z = (T - T_m)/\sqrt{2}\,\sigma$; and $\xi$ is a variable of integration.

The introduction of hypothesis (B) is based on the experimental fact [3] that 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 reenters the lattice. At constant temperature:

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

where $n < m \ll 1$.

At temperatures of the order of 1200°K stoichiometric composition of yttrium oxide is reached only at oxygen partial pressures of $10^{-8}$-$10^{-16}$ Pa [9]. Therefore at oxygen partial pressures in the gas phase of 1 and $0.2 \cdot 10^5$ Pa in our 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, $\Phi_2$. Therefore the temperature dependence $\Phi_2(T)$ is a function not only of temperature, but also of oxygen partial pressure in the gas phase. Unfortunately at present the exact form of $\Phi_2(T)$ is not known, but from the data on electrical conductivity it follows [3] that $\Phi(T)$ 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 diffusional phase transition; over a small temperature range close to the transition point $T_m$ the low temperature phase $Y_2O_3$ + m and the high temperature phase $Y_2O_3$ + n 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 diffusional phase transitions of the first kind [10] predicts that the temperature dependence of the concentration of the transformed phase (and therefore $\Phi_2$) can be approximated by Eq. (14).

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 $\Phi_2$. As an example, Fig. 1a shows the dependence of $\ln D_{eff}$ on 1/T calculated by Eq. (9) with allowance for Eqs. (10)-(13) and at various values of $\Delta H_E$. The low temperature part of the $\ln D_{eff}$—1/T plot is an ascending straight line with slope of $E_2/R$. But 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 variant A, our model predicts the appearance of peaks or plateaus in the $\varepsilon(T)$ curve.

Fig. 1b shows the Arrhenius functions of $D_{eff}$ calculated within the framework of hypothesis (B) (i.e., according to Eq. (9) with allowance for Eqs. (10)-(12) and (14)) at various values of transition width (i.e., of constant $\sigma$). The transition width has a substantial effect on the shape of the emission curves; the narrower the transition, the steeper is the high temperature branch of the peak. In the limit, as 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 emission thermal analysis of yttrium oxide. With the aid of a standard program for nonlinear least squares within the frameworks of hypotheses (A) and (B), the parameters of Eqs. (3), (9), (10)-(12) and (13) (six parameters) and Eq. (14) (nine

theses are suitable for the temperature dependence of the concentration of high temperature complexes. But in the case of model (B) the dispersion, $S^2$, 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 random 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 [3]. Therefore to us hypothesis (B) appears better grounded physically (although this variant contains more parameters so that a longer time is required for data processing). For a final choice of model it is necessary to process the whole collection of existing yttrium oxide ETA curves.

It is of interest to compare the parameters of radon-220 diffusion in yttrium oxide with those of oxygen and yttrium self-diffusion. Published data on self-diffusion in yttrium oxide are extremely limited. Probably the most reliable data have been obtained by heterogeneous isotope exchange of $Y_2O_3$ single crystal with oxygen gas containing $^{18}O$ [11], and by sectioning in the diffusion of $^{91}Y$ in densely sintered $Y_2O_3$ [12]. We did not find any published data on the parameters of noble gas diffusion in yttrium oxide. Table 2 shows the self-diffusion parameters of oxygen [11] and yttrium [12] and the radon diffusion parameters found in the present work. For comparison we show the diffusion coefficients $D_o$, $D_Y$, and $D_{Rn}$ calculated from those parameters at 1673°K.

The last column of Table 2 shows that the high temperature (1673°K) 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.

The published concepts of $Y_2O_3$ defect structure are contradictory. It was recently shown [13] that over a certain range of oxygen partial pressure ($1-0.2\cdot10^5$ Pa), as the temperature is raised the predominant type of ionic defect in the yttrium oxide structure changes; up to ∿1220°K it is mainly $O_i''$, while above 1220°K it is $V_Y''$.

At present it is difficult to determine more specifically the structure of the complexes by which Rn is transferred. Possibly at low temperature it is complex defects of the Willis type [14] in nonstoichiometric uranium dioxide.

On the basis of the work presented here and taking account of the conclusions of [13] it can be concluded that $^{220}Rn$ diffusion in $Y_2O_3$ at temperatures up to ∿1220°K takes place via the easily mobile complex with $O_i''$, participation, while above 1470°K it is via complexes that involve $V_Y''$, and in the intermediate region both mechanisms are present.

## LITERATURE CITED


1. M. O. Marlowe and D. R. Wilder, J. Am. Ceram. Soc., 48, No. 5, 227-233 (1965).
2. R. Kelly and C. Jech, Proc. Br. Ceram. Soc., No. 9, 243-257 (1967).
3. M. D. Lavrov, K. B. Zaborenko, and T. I. Shcherbak, "Electrical conductivity and gas evolution from yttrium oxide," All-Union Institute of Scientific and Technical Information, Academy of Sciences of the USSR, deposited paper No. 2165-77 (June 2, 1977).
4. K. E. Zimens, Z. Phys. Chem., Part A, 192, 1-55 (1943).
5. K. B. Zaborenko, L. L. Melikhov, and V. A. Portyanoi, Radiokhimiya, 7, No. 3, 319-324 (1965).
6. T. I. Shcherbak and K. B. Zaborenko, Radiokhimiya, 21, No. 6, 894-899 (1979).
7. Radiography [collection of articles translated from English], Inostr. Lit., Moscow (1952), p. 164.
8. F. Van der Maesen and J. A. Brenkman, J. Electrochem. Soc., 102, No. 5, 229-234 (1955).
9. P. A. Arsen'ev. L. M. Kovba, Kh. S. Bagdasarov, et al., Compounds of Rare Earth Elements [in Russian], Nauka, Moscow (1983), pp. 55-60.
10. A. V. Tobol'skii and N. G. Konter, in: Transitions and Relaxation Phenomena in Polymers (B. Roiter, editor) [Russian translation], Mir, Moscow (1968), p. 30.
11. K. Ando, Y. Oishi, H. Hase, and K. Kitazawa, J. Am. Ceram. Soc., 66, No. 12, C 222-223 (1983).

12. M. F. Berard and D. R. Wilder, J. Am. Ceram. Soc., 52, No. 2, 85-88 (1969).
13. Ken Hong Kim, Sung Ho Park, and Jae Shi Choi, Taehan Huahakhoe Chi, 28, No. 3, 149 (1984).
14. G. E. Murch, D. H. Brandhurst, and H. J. de Bruin, Phil. Mag., 32, No. 6, 1141-1150 (1975).

# DETERMINATION OF AMERICIUM AND CURIUM BY ISOTOPE DILUTION

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During the reprocessing of spent fuel from water-cooled water-moderated power reactors, significant difficulties can appear in the determination of americium and curium in highly radioactive solutions. The use of alpha-spectrometric methods for these purposes is complicated because of the high level of beta and gamma radiation and also because of the presence of radionuclides whose alpha-radiation energies are close to the alpha-radiation energies of americium and curium.

For recovery and purification of americium and curium from solutions of different compositions, methods have been recommended which are based mainly on extraction by organophosphorus compounds, especially bis(2-ethylhexyl) orthophosphate (B2EHP) [1]. The use of the mentioned methods for analytical purposes does not ensure quantitative recovery of americium and curium; therefore, to determine their yield we used one of the variants of the isotope-dilution method [2]. The essence of the proposed method of analysis consists in the fact that simultaneous recovery of americium and curium is carried out from two portions of the solution being analyzed, to one of which is added as a label a known amount of the $^{241}$Am radionuclide; the relative content of americium and curium is determined by alpha spectrometry.

To carry out the proposed variant of the isotope-dilution method, it is necessary that separation of these elements not occur during the purification of americium and curium. Preliminary experiments indicated that the alpha-spectrometric characteristics of the starting solution of $^{241}$Am and $^{244}$Cm and the eluate of Am and Cm were identical after their extraction-chromatographic recovery, i.e., fractionation of the mentioned elements did not occur. In this case, the correlation of the numbers of alpha decays of $^{244}$Cm ($N_4$ and $N_4'$) and $^{241}$Am ($N_1$ and $N_1'$) contained characteristically in the solution being analyzed should be constant for both samples. Therefore, we can write

$$N_1' = N_4' \frac{N_1}{N_4}.$$

Then, after recovery, the number of alpha decays $N_1^*$ due to the alpha radiation of $^{241}$Am added to the sample as a label will be equal to

$$N_1^* = N_1'' - N_4' \frac{N_1}{N_4},$$

where $N_1''$ is the number of alpha decays due to alpha radiation of $^{241}$Am present in the solution being analyzed and added to the sample as a label ($N_1^* + N_1'$).

Therefore, the chemical yield of $^{244}$Cm and $^{241}$Am can be calculated according to the equation

$$Z = \frac{N_1^*}{N_1^0} = \frac{N_1^0 - N_4' \frac{N_1}{N_4}}{N_1^0} = \frac{\frac{N_1''}{N_4'} - \frac{N_1}{N_4} N_4'}{N_1^0},$$

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