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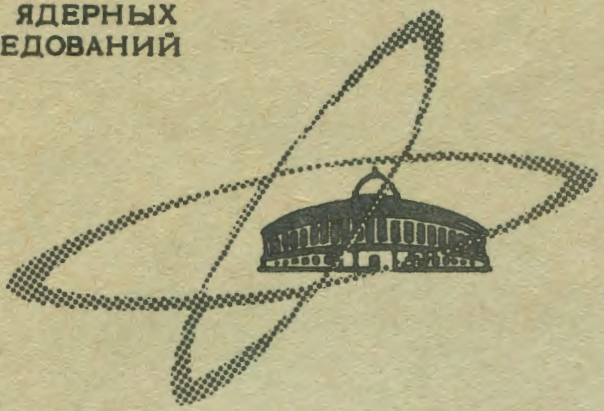

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THERMAL ANNEALING OF THE RADIORHENIUM RECOILS FORMED BY THE HIGH ENERGY PROTON IRRADIATION OF AMMONIUM PERRHENATE

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1. Introduction

The previous results obtained by us and unpublished till now show that the behaviour of radiorhenium atoms in thermal annealing processes in sodium perrhenate and potassium chlororhenite irradiated with high energy protons depends on the chemical aggregate state of the irradiated compound and on the conditions of irradiation and annealing.

Our results showed that the thermal annealing of rhenium in crystalline sodium perrhenate and potassium chlororhenite involved processes of a different nature. The isothermal annealing process in sodium perrhenate involves the reduction and oxidation reactions of radiorhenium but in the potassium chlororhenite the classical isothermal annealing curves were obtained.

The present work using ammonium perrhenate irradiated with high energy protons was initiated to investigate the isothermal annealing process.

Until now many authors studied the chemical behaviour of recoil atoms in neutron irradiated ammonium compounds/1-9/. Generally the irradiated ammonium salts of oxyanions show somewhat lower retention than the corresponding alkali metal salts. Harbottle and Sutin/10/ have sug-

gested that this might be due to the reduction of the recoil fragments by ammonium ions.

Some results reported up till now showed that the ammonium group in a compound can influence the course of thermal and radiation annealing/8/. It was concluded that the effect was caused by the reducing properties of the hydrazine originating from the ammonium group.

The initial retention values of crystalline perrhenates of sodium, potassium and ammonium irradiated in the same conditions with 660 MeV protons were determined. R_0 values found for perrhenates of sodium, potassium and ammonium are respectively: 96, 98 and 67%. As is seen there is a difference in R_0 values obtained for alkali metal perrhenates and ammonium perrhenate.

The results obtained by studying the annealing processes in alkali metal and ammonium salts irradiated with neutrons showed that the annealing behavoiour of recoil atoms depends on the chemical composition of the irradiated compound. We considered it interesting to compare thermal annealing processes occurring in sodium and ammonium perrhenates irradiated with protons of high energy. This is done in order to investigate the effect of the ammonium group on the annealing behaviour of radiorhenium in crystalline oxy-anions irradiated with protons at 660 MeV.

II. Experimental

Analytical reagent quality ammonium perrhenate recrystallised three times was used. Radiorhenium was obtained as a product of 660 MeV proton irradiation of ammonium perrhenate by nuclear reaction $Re(p, pxn)Re$. Samples were placed in aluminium containers and irradiated

in the external beam of the Dubna synchrocyclotron. The temperature during irradiation did not rise above 30°C. The intensity of the proton beam was 10^8-10^{10} p/cm^2·sec for whose determination use was made of the yield of ^{24}Na formed in the $^{27}Al(p, 3pn)^{24}Na$ reaction.

For the isothermal annealing experiments, definite amounts of irradiated ammonium perrhenate were placed in open glass ampoules in an electric oven at different temperatures. Throughout the period of heating the temperature of the oven was constant at 1°C.

The distribution of radiorhenium between two stable valences. of Re-IV and Re-VII was studied. Rhenium -VII was separated from Re-IV by precipitation only of Re-VII as Re_2S_7 from the (4 M HCl) acid solution. For the purification of rhenium chemical forms known methods were used.

III. Results and Discussion

The changes of retention in the thermal annealing process depending on experimental condition like temperature, time of heating, intensity of the proton flux are shown in Figs. 1,2 and 3. As can be seen from results presented, the retention of ammonium perrhenate was not found to follow a typical annealing process. The effect of the temperature on retention for ammonium perrhenate irradiated at a constant flux of protons is shown in Figs.1 and 2. The annealing isotherms for ammonium perrhenate irradiated at different fluxes are given in Fig.3 and 4. It may be seen from Figs. 1, and 2 that the annealing isotherms present certain irregularities. Upon increasing the temperature the irregularities presented by the anne-

aling curves become prominent. As is seen from Figs.1 and 2 upon increasing the temperature the tendency to shift the maxima to the shorter time of heating is pronounced.

The results presented in Fig.3 show that the intensity of the proton flux influenced the shape of the annealing curve. Comparing the results presented in Figs. 1,2 and 3 it may be said that ammonium perrhenate is very sensitive to the conditions of proton irradiations. A high intensity of the proton flux emphasized the irregularities of the annealing processes. A comparison between Figs.1 and 2 shows the different pattern of the annealing process. For a higher intensity of the proton flux a more complicated shape was obtained (Fig.2). In this case the proton bombardment produced some darkening of crystals. The coloration was not intensified by heating in our conditions.

The irregularities of the annealing isotherms show the competing oxidation and reduction reactions occurring in the irradiated crystals of ammonium perrehenate.

It is possible to assume that the decrease of retention is a result of interaction of recoil rhenium containing fragments with some lattice defects responsible for the reduction process.

It is also possible to suppose that this behaviour of annealing retention is due to radiolitic phenomena and to partial thermal decomposition of the ammonium perrhenate/11/. As is seen from Figs. 1,2 and 3 the higher the temperature and the intensity of the proton flux the higher the probability of competing reactions to occur.

A comparison between the annealing isotherms obtained in sodium perrhenate and ammonium perrhenate is given in Fig.4. As is seen from Fig.4, the reduction of radiorhenium by the annealing process of sodium perrhenate is very slight. The retention decreases over a time of 30 minutes

and reaches a value that remains practically constant fo 6 hours of heating. In the same experimental conditions th annealing pattern for ammonium perrhenate is more complica ted. The retention at first dicreases and after about 30 mi nutes begins to increase, reaches a maximum and after hours again begins to decrease.

It may be that the reduction and oxidation processe of rhenium recoils take place in solid state and also i solution. The concurrent reactions are due to the interac tion of rhenium recoils with some lattice defects create by nuclear transformation and with radiation-produced ra dicals.

The experimental evidence shows that radiorheniu atoms formed by proton irradiation of ammonium perrhenat crystals appear in valency forms which are affected by th redistribution of negative and positive vacances in ther mal annealing processes.

It is possible also that due to the recoil energy fre radical and metastable fragments are formed from the ammo nium group. These are then available for the reaction wit the recoil atoms. In addition to this the ammonium grou can be transformed in certain reducing compounds. Thi step could occur either during the irradiation and/or i the annealing process/8/.

Owing to the complexity of such phenomena it seems t be very difficult to determine the kinetic analysis o these curves.

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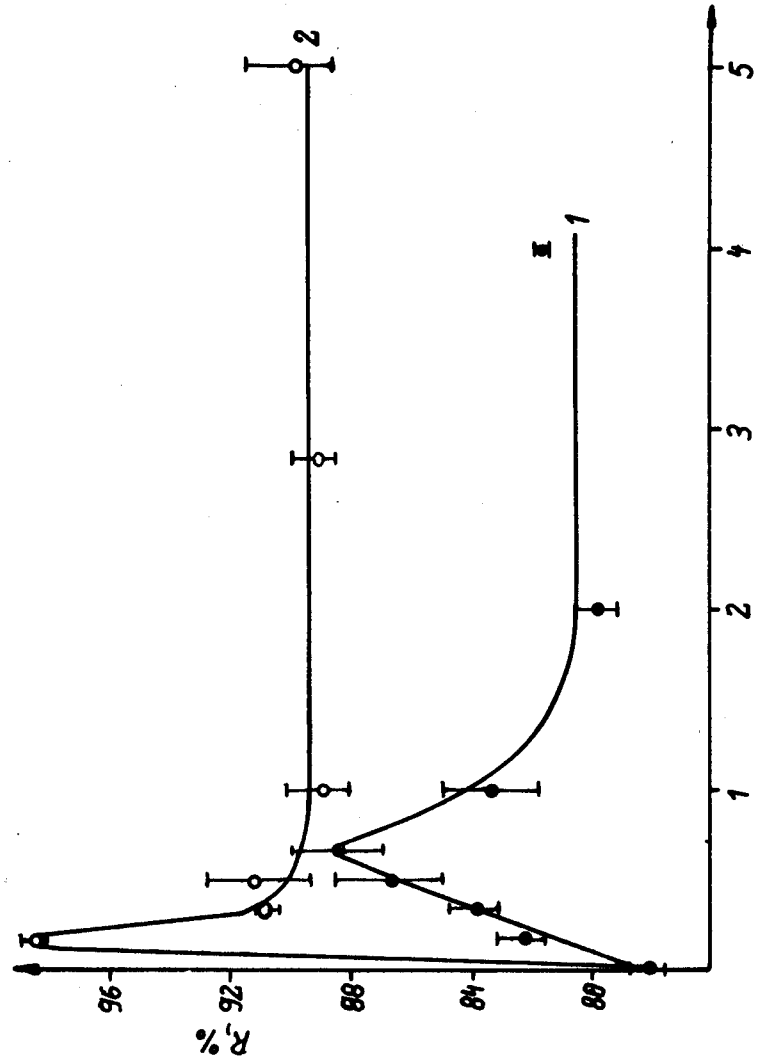

Fig.1. Isothermal annealing curves for ammonium perrhenate irradiated with protons at 660 MeV ($\phi = 1.36 \cdot 10^{10}$ p/cm^2 sec) 1 -50^{o}C: 2-100^{o}C.

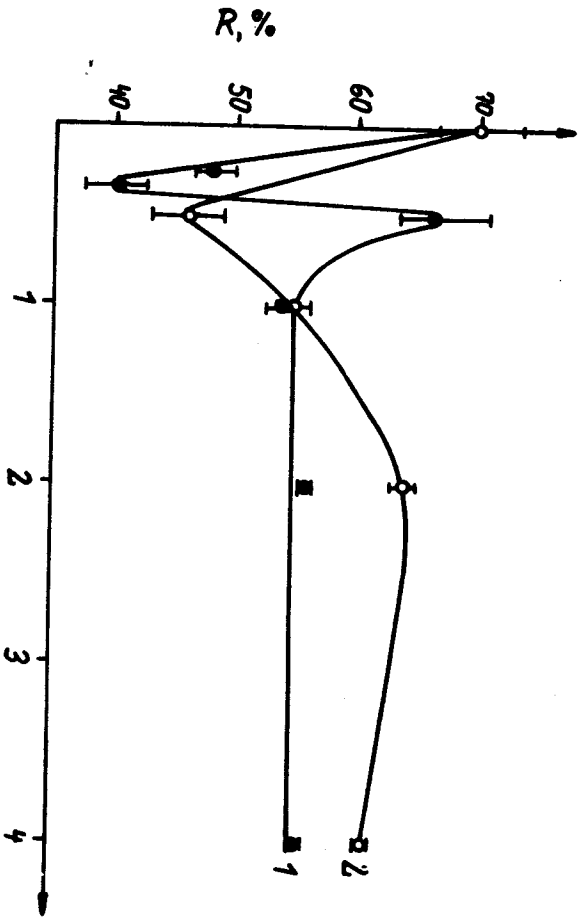

Fig.2. Isothermal annealing curves for ammonium perrhenate irradiated with protons at 660 MeV ($\phi = 2.43.10^{10}$ p/cm^{2}sec) 1-200°; 2 - 100°C.

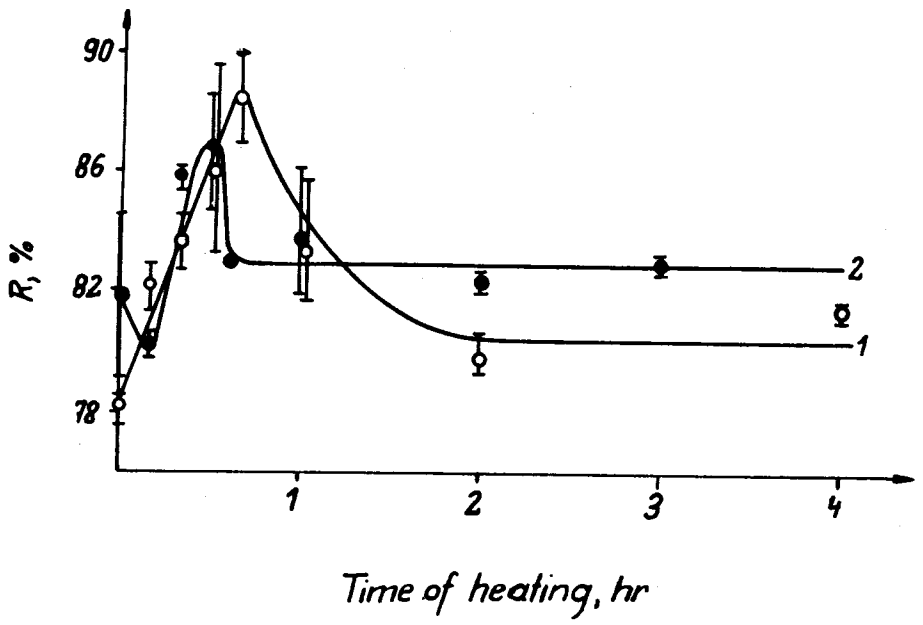

Fig.3 Isothermal annealing at 50°C for ammonium perrhenate irradiated with protons at different fluxes. 1 - ϕ = $1.36.10^{10}$p/cm^{2}sec 2- ϕ = $3.79.10^{10}$p/cm^{2}sec.

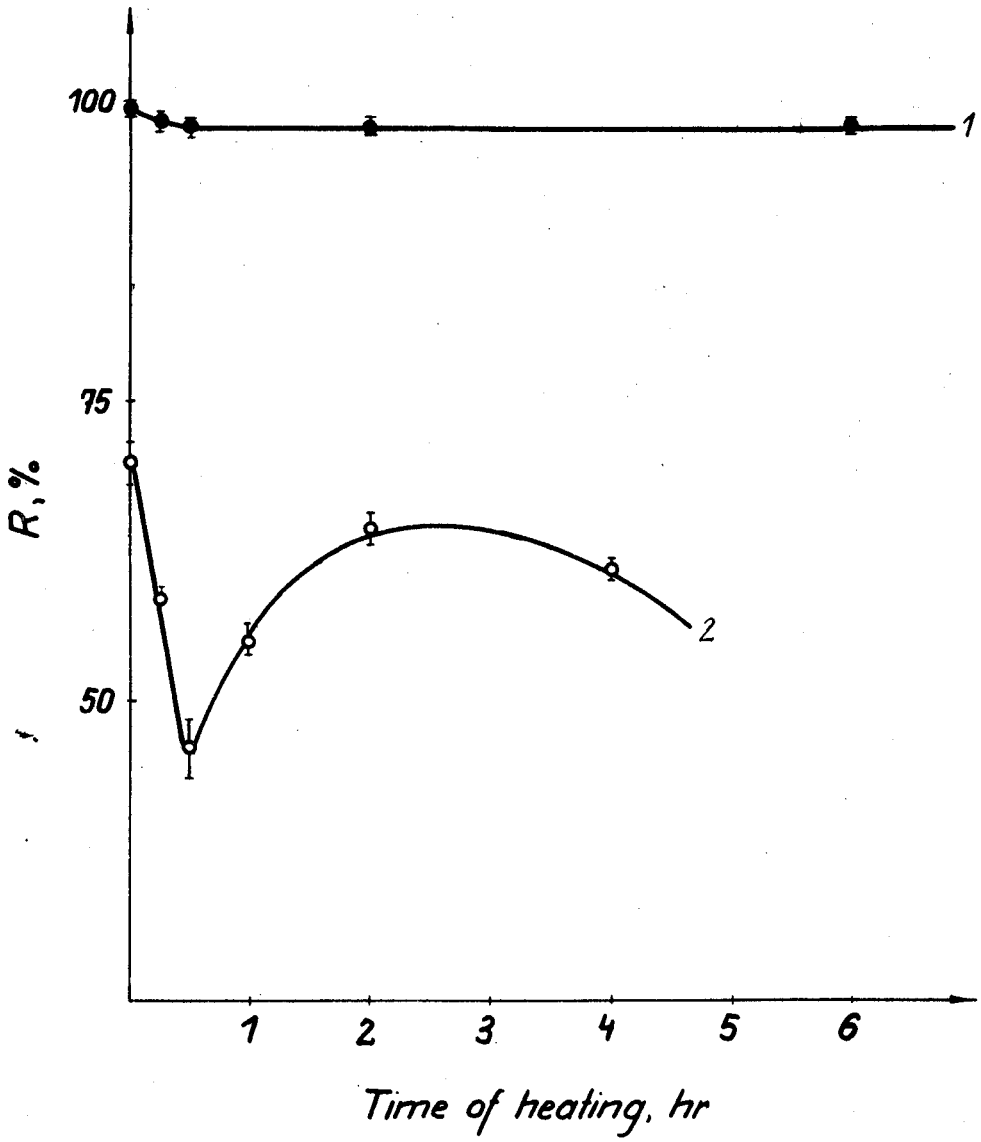

Fig.4. Isothermal annealing curves at 100°C for sodium perrhenate and ammonium perrhenate irradiated with protons at 660 MeV. 1 - $NaReO_4$; $\phi = 2.86 \times 10^{10}$ p/cm^2.sec. 2 - NH_4ReO_4 ; $\phi = 2.43 \times 10^{10}$ p/cm^2. sec.