СООБЩЕНИЯ
ОБЪЕДИНЕННОГО
ИНСТИТУТА
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

E6 - 4916

E. Ianovici, N. Zaitseva

ЛАБОРАТОРИЯ ЯДЕРНЫХ ПРОБЛЕМ

THERMAL ANNEALING BEHAVIOUR OF RADIORHENIUM RECOILS FORMED BY HIGH ENERGY PROTON IRRADIATION OF SODIUM HEXACHLOROIRIDATE

1970

E6 - 4916

E. Ianovici, N. Zaitseva

THERMAL ANNEALING BEHAVIOUR OF RADIORHENIUM RECOILS FORMED BY HIGH ENERGY PROTON IRRADIATION OF SODIUM HEXACHLOROIRIDATE

The chemical forms of stabilized atoms of radorhenium formed by the $Ir(p,3pxn)Re$ nuclear reaction have been reported earlier/1,2/. The results obtained showed the important role of the chemical environment on the fate of the recoil atom. Thus for hydrated and anhydrous sodium salts and for ammonium salt the following decrease of the yield of Re(VII) was found:

$$Na_2IrCl_6 \cdot 6H_2O > (NH_4)_2IrCl_6 > Na_2IrCl_6 .$$

That shows the oxidizing role of water of crystallization and ammonium ion. It was shown that in Na_2IrCl_6 the yield of radiorhenium found in the heptavalent state increases with the increase of the radiation dose.

The present work was initiated to investigate the thermal annealing behaviour of radiorhenium recoils formed by irradiation of anhydrous sodium hexachloroiridate with 660 MeV protons. The roles of irradiation-induced defects and inherent crystal defects in the annealing process are examined. The results are analysed from the point of view of the kinetics of the process; the order of reaction is determined and the activation energy is calculated.

Experimental

Anhydrous Na_2IrCl_6 crystals were obtained by drying the hexahydrated salt $Na_2IrCl_6 \cdot 6H_2O$ in a vacuum desiccator over 97% H_2SO_4 solution.

The irradiation was performed at room temperature in the external beam of the Dubna synchrocyclotron, the crystals being sealed into glass ampules in vacuo. The proton beam intensities for whose determination use was made of the yield of ^{24}Na formed in the $^{27}Al(p,3pn)^{24}Na$ reaction are the following: 8.9×10^9 p/cm^{2}sec and 2.1×10^{10} p/cm^{2}sec (Figs. 1 and 2) and 1.7×10^9 p/cm^2 sec (Fig.3). For the thermal annealing experiments quantities of about 20 mg of the irradiated compound were heated in glass ampules in an electric oven. Fluctuation in temperature amounted to less than 1°. Experiments in vacuo were conducted by annealing in the irradiation ampules.

The annealing process was studied by observing only the fraction of radiorhenium found in the heptavalent state. The analytical procedure and radioactive measurements employed were described earlier[1,2].

Results

a) *Thermal Treatment*

The variation of the yield of radiorhenium found in the heptavalent state with the time of heating at different temperatures is shown in Fig.1. As is seen, the typical annealing curves are obtained. An increase of the yield of Re(VII) with temperature is observed, the isothermal curves each reach a pseudo-plateau which is dependent on temperature.

Fig.2 presents the isotherms at 320°C for sodium hexachloroiridate irradiated at different proton fluxes. It may be seen that a higher flux causes a larger radiorhenium oxidation. The results presented in Fig.2 show that the irradiation-induced defects have a marked influence on subsequent recoil annealing.

The effect of heating of crystals before the proton irradiation on the subsequent recoil annealing was studied. This was done in order to verify if inherent crystal defects initially presented as a bulk property of the lattice are involved in the recoil annealing process.

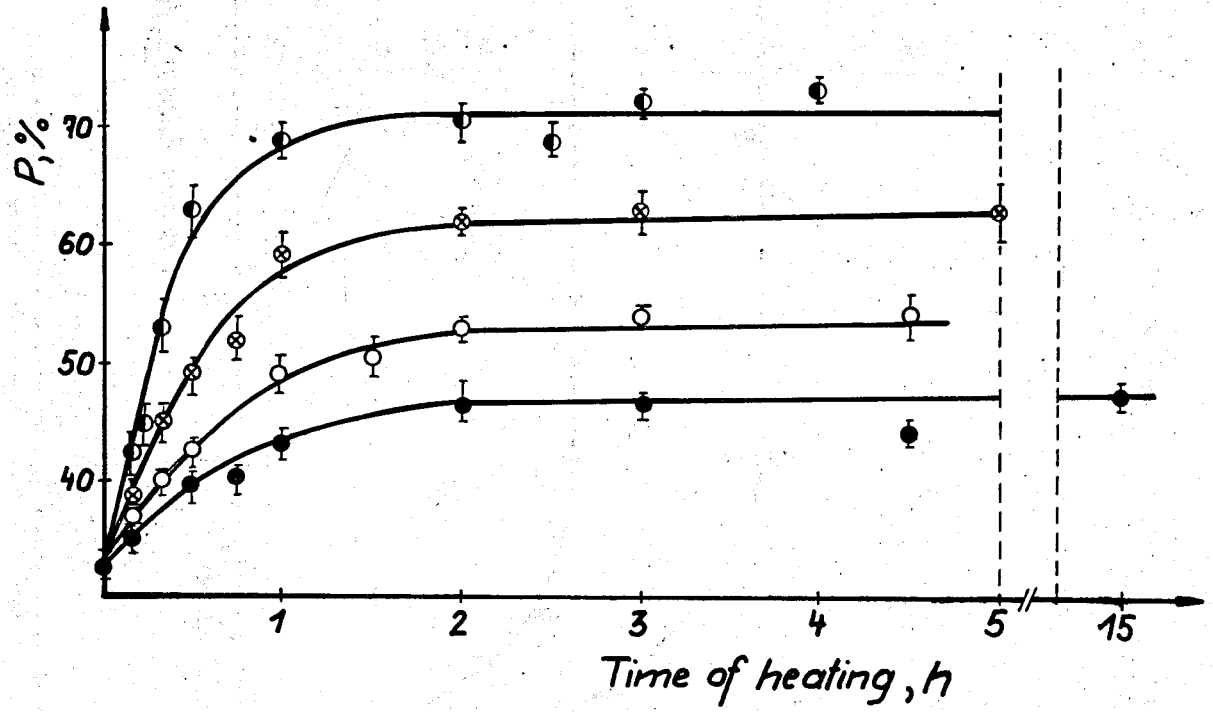

Fig.1. The yield of Re(VII) as a function of the thermal annealing time in Na_2IrCl_6 (ϕ = 8.9×10^9 p/cm^{2}sec).

● - 200°; ○ - 250°; ⊗ -320°; ◐ -350°C.

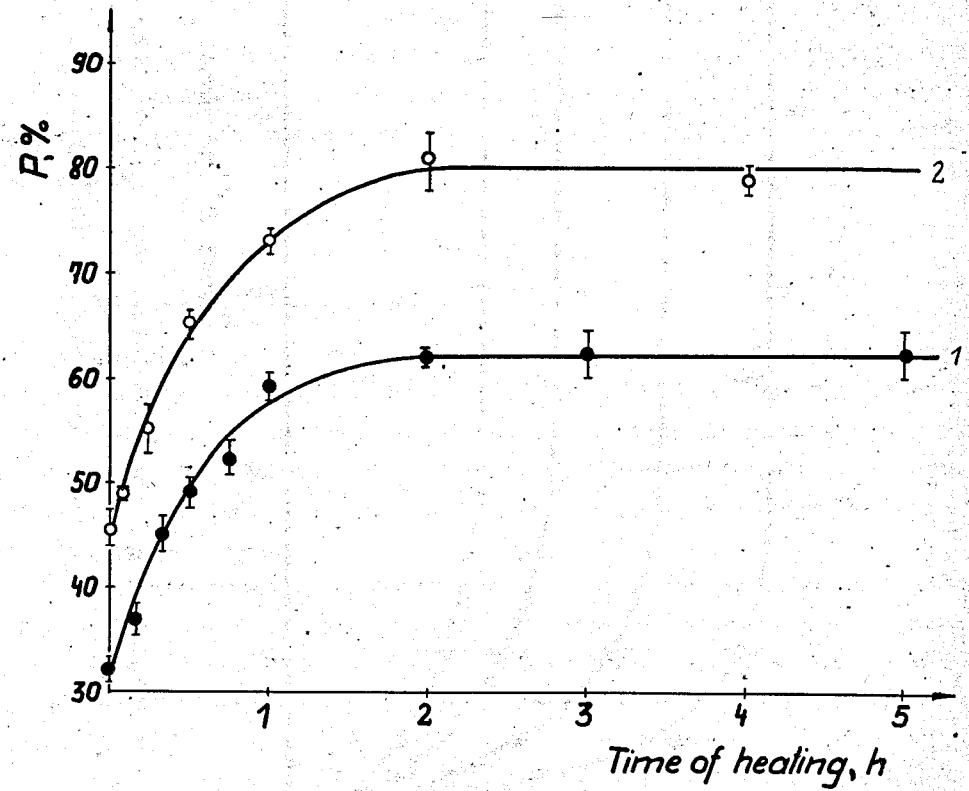

Fig.2. The yield of Re(VII) as a function of the isothermal annealing time at 320° in Na_2IrCl_6 irradiated at different proton fluxes 1 - ϕ = 8.9×10^9 p/cm^2 sec; 2 - ϕ = 2.1×10^{10} p/cm^{2}sec.

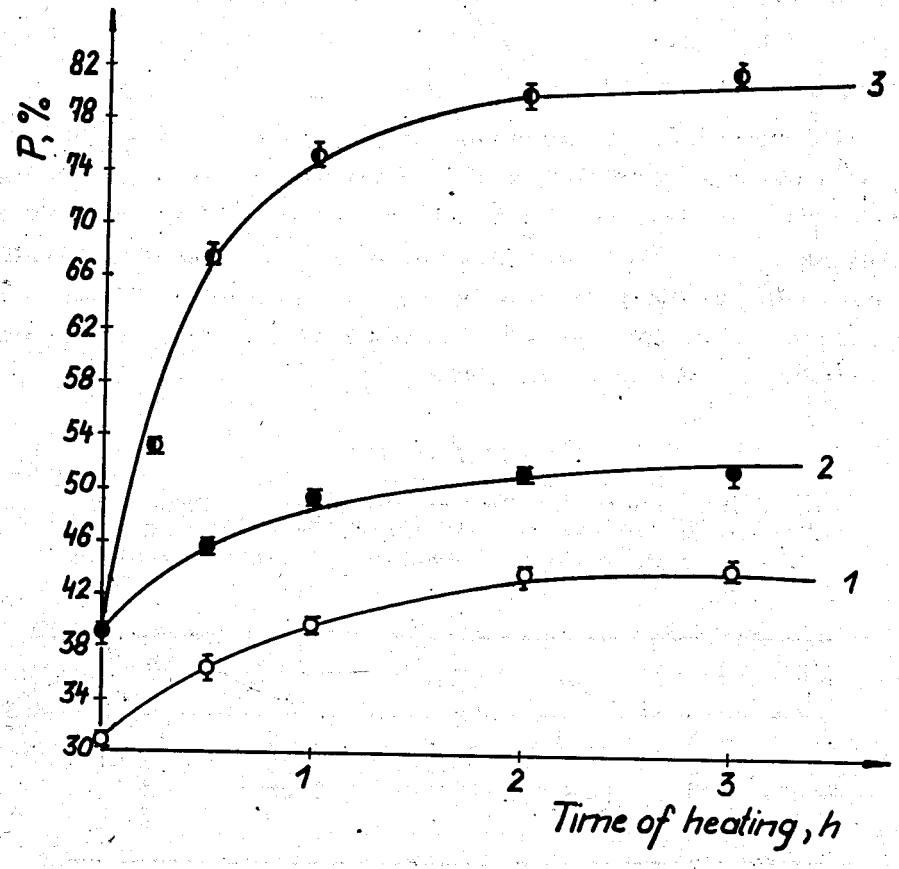

Fig.3. The yield of Re(VII) as a function of the isothermal annealing time in Na_2IrCl_6 (ϕ = 1.7×10^9 p/cm^{2}sec).
1 - samples untreated before irradiation;
2 - samples heated at 200° for 2 hr before irradiation;
3 - samples untreated before irradiation, but annealed in vacuo.

Fig.3 presents the isotherms at 200°C corresponding to a sample heated 2 hours at 200°C before the irradiation -curve 1 and not pre-irradiated heated - curve 2.

Fig.3 also represents the isotherm of a sample annealed in vacuo - curve 3. It can be seen that pre-irradiated heating decreases the initial yield of Re(VII) and lowed the plateau value of the annelaing isotherms. As is seen from Fig.3, for the same temperature a higher yield of Re(VII) is obtained for the sample heated in the absence of the air.

b) Kinetic Analysis

The annealing data presented in Fig.1 were analysed in order to obtain the rate of transition of rhenium from lower to higher oxidation form. The plots of $\log(P_\infty - P_t)$, where P_t is the yield of Re(VII) after a specific time of heating and P_∞, the yield of Re(VII) corresponding to the pseudo-plateau, versus time of heating, were analysed to obtain the rate and the order of the oxidation reaction. The results are presented in Table 1.

Table 1

Kinetic parameters for thermal annealing of the radiorhenium recoils in high energy proton irradiated sodium hexacloroiridate

t°C	P_o %	P_∞	$\Delta P = P_\infty - P_o$	$t_{1/2}$ sec^{-1}	$K \times 10^{-4}$ sec^{-1}
200	32.5	46.5	14.0	1560	4.45
250	32.5	53.0	20.5	1440	4.81
320	32.5	62.0	29.5	1200	5.77
350	32.5	71.5	39.0	960	7.22

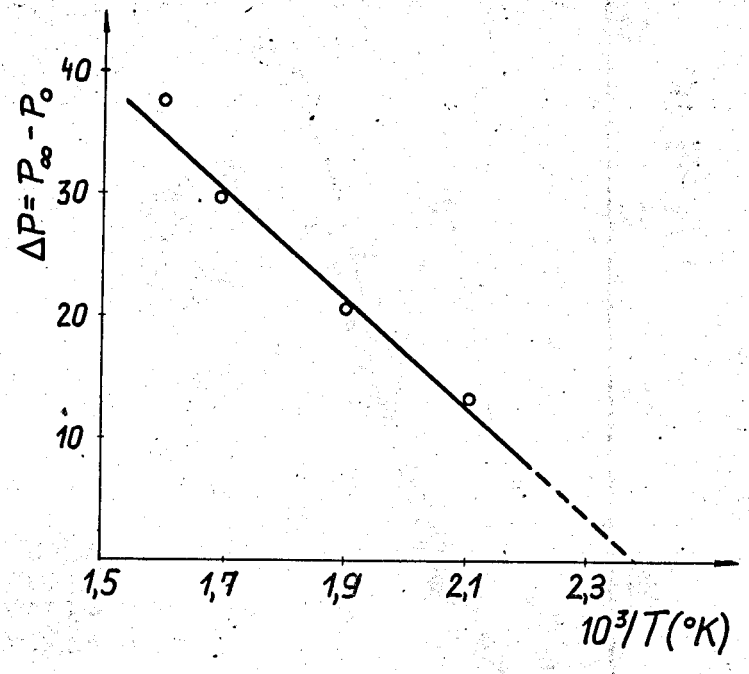

Fig.4. Increase in Re(VII) yield to the pseudo-plateau, ΔP, as a function of the absolute temperature.

Fig.4 shows the temperature dependence of the annealed fraction taking into account the pseudo-plateau value. A linear dependence is obtained, as it has been observed also in the other studies. From Fig.4 it was found that the temperature at which the annealing begins is 147°C.

Some information about the processes taking place in the thermal annealing can be obtained from calculation of the activation energy. The activation energy has been calculated by method of Vand and Primak/4,5/. It was therefore considered that the processes are distributed in activation energy which is of the type, $E_0 = k\,T\,\ell n\,(B\,t)$. Fig.5 represents the fraction of radiorhenium recoils annealed $P = P_t - P_0$ where P_0 means the initial yield of radiorhenium in higher oxidation form and P_t the same yield at various times of heating, versus E_0. The best superposition of experimental values was obtained with a

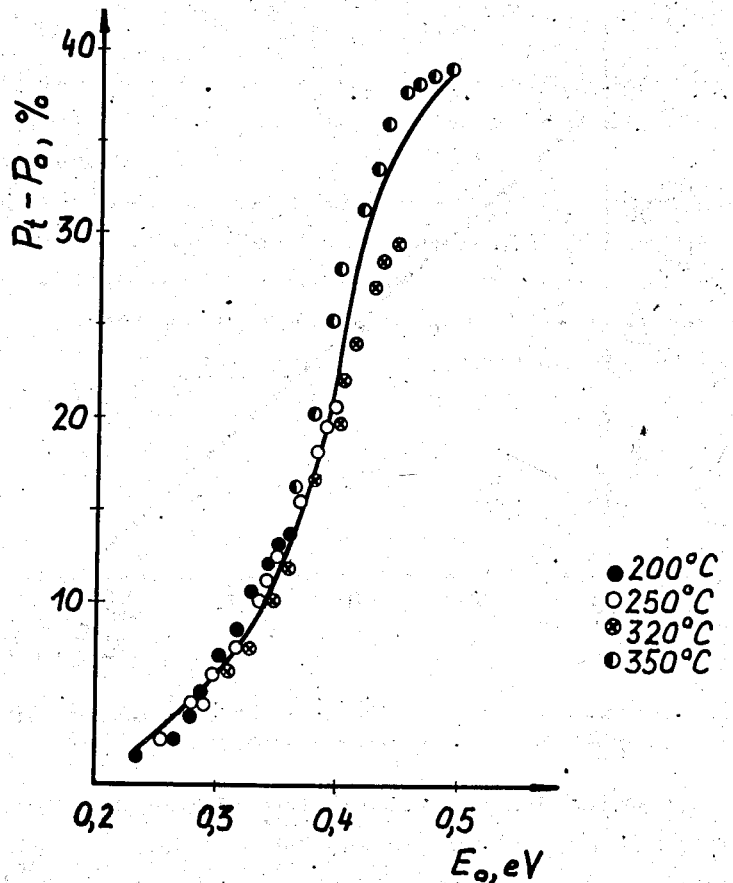

Fig.5. The initial distribution of the annealing process in activation energy.

value for the frequency factor $B = 1\ sec^{-1}$. In Fig.6 was plotted the studied property in the form $P_0 = dP/dE_0$, where $P = P_t - P_0$ versus activation energy (E_0). From Fig.6 it may be seen that for the studied case a continuous spectrum with a Gaussian shape is obtained. The distribution of activation energies is spreaded between 0.2 - 0.5 eV with the peak position at 0.4 eV.

Reaction orders and also activation energy can be obtained by the method of Fletcher and Brown[6]. It is known that the annealing is a function of t/τ, where τ is the average jump-time given by

$$\tau = \nu_0^{-1} \exp(E/kT).$$

It is possible to superimpose the annealing curves for different temperatures by adjusting the time scales by proper factors.

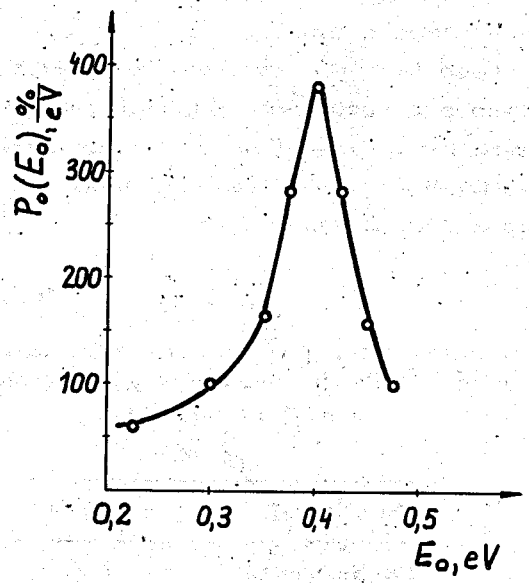

Fig.6. Activation energy spectra.

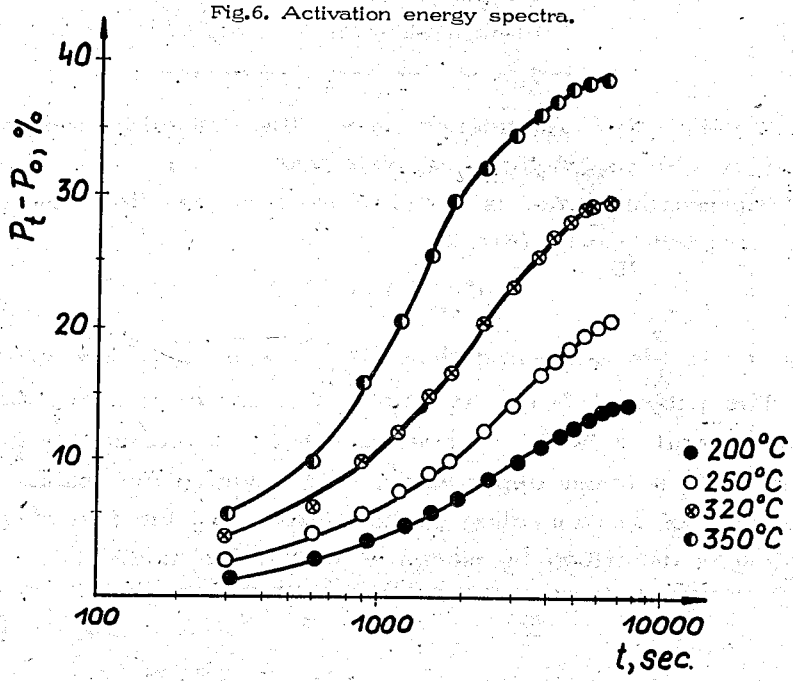

Fig.7. Kinetic curves of the thermal annealing process.

Fig. 7 presents the curves of the annealing process rate as a function of the time of heating. The composite curve for the plot of heptavalent rhenium fraction against $\ln t'$ ($t' = t_{320°C}$) is shown in Fig. 8. As it is seen from Fig.8 for the fast stage of the annealing a satisfactory composite curve was obtained. By plotting the multiplicative factors used for obtaining the composite annealing curve versus $1/T$, the activation energy was obtained (Fig.9). The results obtained are presented in Table 2.

Table 2

Activation energy for the thermal annealing of the radiorhenium recoils in high energy proton irradiated Na_2IrCl_6

Method	E , eV
Vand-Primak	0.40
Fletcher-Brown	0.30

A very good coincidence among the activation energies calculated by the two methods is observed.

The reaction order is obtained from the equation corresponding to the composite curve (Fig.8)

$$P = P_{max} (1 - e^{-kt}),$$

where t is the annealing time, $P_{max} = 38$ and $k = 3.7 \times 10^{-4}$.

The plots of $\ln t$ versus $1/T$ for a constant degree of annealing and of $\ln (P_t - P_0)$ versus $1/T$ for a constant time of heating show a linear dependence. In conclusion the results obtained by analysis of the annealing process show that the fast stage of the annealing is described by means of first order kinetics.

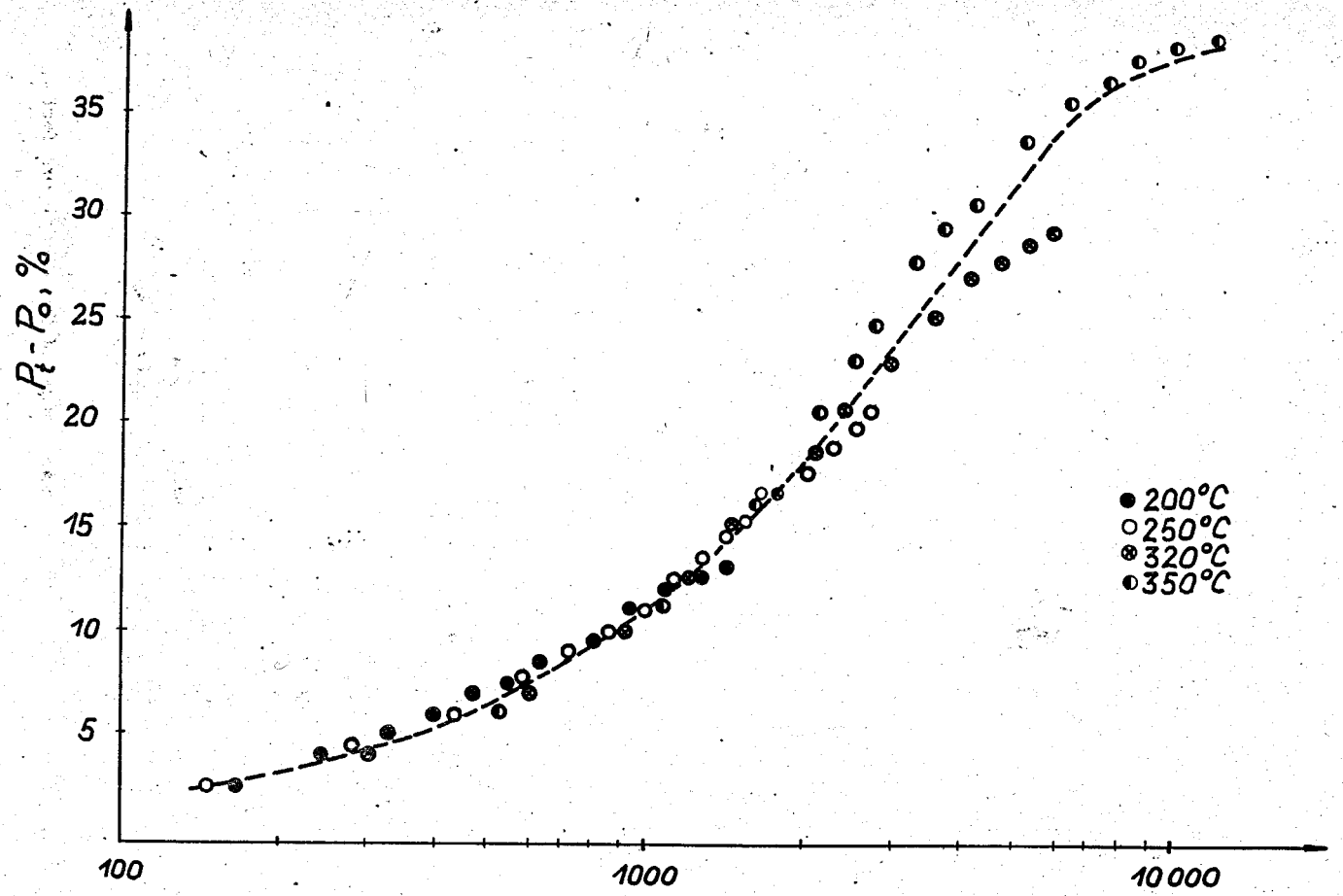

Fig.8. Composite annealing curve with respect to the curve at 320°C.

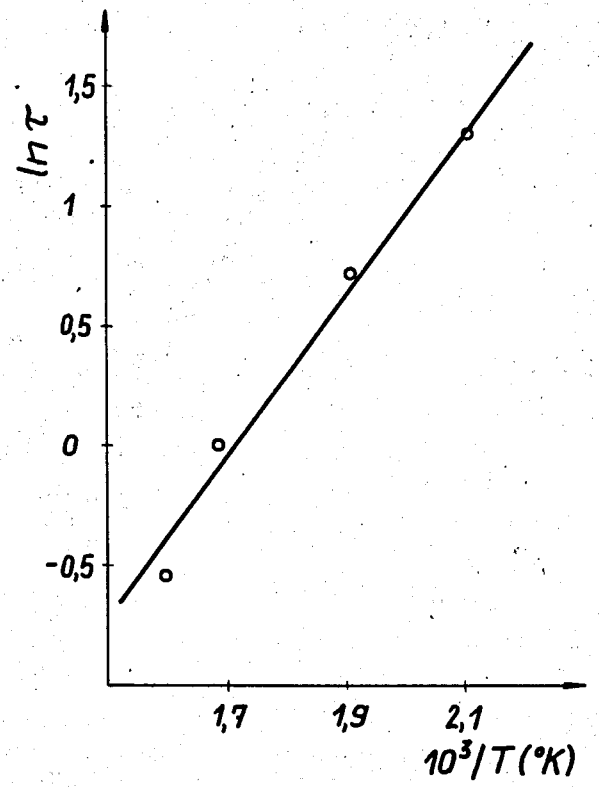

Fig.9. Variation with the absolute temperature of the adjustment factor.

Discussions

The results presented in Figs. 1,2,3 show an oxidation process of the radiorhenium recoils by heating.

Baumgartner and Maddock[7] have suggested that the oxidative annealing comprises a step of removel of an electron from the radioactive fragment followed by a recombination process involving the radioactive fragment and its surrounding. As by thermal annealing of sodium hexachloroiridate an oxidation process takes place, a release of an electron from the radiorhenium recoils can be expected. This process requires some acceptor sites in the vicinity of the radioactive fragment. The defects normally presented in the crystallites as well as those induced by irradiation and formed in the track of the recoil atom can form acceptor sites.

It was shown above (Fig.2) that the higher the intensity of the proton flux, the larger the yield of Re(VII) . It can be supposed that by irradiation some kind of defects with oxidizing character is formed. It is to expect that the oxidation of the radiorhenium by heating will depend upon its interaction with irradiation-induced defects which can form " electron traps".

As in the case of Na_2IrCl_6 the oxidative annealing reaction of the radiorhenium was partially annihilated by heating, it can be supposed that the defects inherent of the crystal in part responsible for the annealing were removed by thermal treatment before irradiation. Some oxidative annealing was still observed. This means that defects and/or radiolitic products produced by irradiation take part in the annealing process.

If the release of electrons is responsible for thermal annealing then the annealing process could be affected by electron donating or electron accepting ambiant gases. Our results (Fig.3) show that in the absence of air the magnitude of anneal increases considerably. Earlier it was reported[8] an oxigen effect on the annealing process for some cobolt complexes. The authors supposed that the oxigen absorbed on the surface acts as electron traps and suppresses the annealing.

It was shown[9,10] that the activation energy of the thermal annealing decreases in proportion as the samples underwent a more intense radiation flux. It was also reported that the sensitivity at the thermal annealing is the greater, the more intense is the flux undergone by the samples. The decrease of the activation energy was related with defects concentration. The influence of the defects on the annealing process was reported earlier[11]. Some experiments led to the idea that the vacancies produced during the irradiation promote the annealing process[12]. The above idea and the results presented in Fig.2 give us the possibility to suppose that the activation energy value of 0.3-0.4 eV found for the annealing of the radiorhenium recoils in Na_2IrCl_6 is at least partially determined by the magnitude of the proton flux.

References

1. *E. Ianovici and N. Zaitseva. J. Inorg.Nucl.Chem., (in press).*
2. *E. Ianovici. Thesis, Leningrad, 1969.*
3. *M. Delépine and P. Boussi. Bull.Soc.Chim. Fr., 23, 278 (1918).*
4. *V. Vand. Proc.Phys.Soc., 55, 222 (1943).*
5. *W. Primak. Phys.Rev., 100, 1677 (1955).*
6. *R.C. Fleitcher and W.L. Brown. Phys.Rev., 92, 585 (1953).*
7. *F. Baungartner and A.G. Maddock. Trans.Farad.Soc., 64, 714(1968).*
8. *A. Nath, K.A. Rao, V.G. Thomas. Radiochim.Acta, 3, 134 (1964).*
9. *M.M. Maine, A.G. Maddock and K. Taugbol. Trans.Faraday Soc., 23, 211 (1957).*
10. *T. Costea and I. Negoescu. Rev.Roum.Phys., 10, 561 (1965).*
11. *A.G. Maddock and J.I. Vargas. Nature, 184, 1931 (1959).*
12. *A.G. Maddock, F.E. Treloar and J.I. Vargas. Trans. Faraday Soc., 59, 924 (1963).*

Received by Publishing Department
on February 5, 1970.